The Modification of Gold Surfaces via the Reduction of Aryldiazonium Salts

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Abstract

This thesis presents the study of films derived from the reduction of aryldiazonium salts at gold surfaces. The properties of bare polycrystalline surfaces were investigated via the observation of the electrochemical oxidation and reduction of the gold. Films derived from diazonium salts were electrochemically grafted to the gold surface. The structure and stability of these interfaces was examined through the use of redox probes, gold oxide electrochemistry and water contact angle measurements. The spontaneous reduction of aryldiazonium salts at gold surfaces was investigated and the possible applications it presented towards printing and patterning of the gold surface with films were explained.

Polycrystalline gold surfaces were prepared and subjected to various treatments, to observe the behaviour of gold oxide formation and reduction at the surface. Various effects on the surface structure were observed after treatment in solvents and electrolyte solutions. The surface structure of the gold atoms frequently changed due to the high mobilities of the gold atoms, and it is difficult to achieve a reproducibly stable surface.

The electrochemical modification of gold surfaces via the reduction of aryldiazonium salts was investigated. Surfaces were modified with methylphenyl and carboxyphenyl films and exposed to various treatments. Monitoring the gold oxide reduction changes enabled the surface coverage of modifier directly attached to the surface to be calculated. The films appear to be stable, loosely packed and porous. The films are flexible in nature; redox probe responses showed reversible changes after repeated sonication in solvents of

differing polarities and hydrophilicities. Contact angle measurements further support the notion of films that can reorganise in response to their environment.

The spontaneous reduction of aryldiazonium salts at gold surfaces was observed. Film coverage was significantly lower at the spontaneously grafted surface than for films grafted electrochemically. Gold surfaces were successfully modified via microcontact printing, and surface coverages similar to the spontaneously grafted film were achieved. Microcontact printing was also used to pattern surfaces with films derived from diazonium salts. Feature sizes down to 100 μm were successfully achieved.

Abbreviations

ACN	Acetonitrile
AFM	Atomic Force Microscopy
Ar	Aryl ring
CB	Carboxybezene
CP	Carboxyphenyl
CV	Cyclic Voltammetry
DMF	Dimethylformamide
E	Potential
EIS	Electrochemical impedance spectroscopy
EQCM	Electrochemical quartz crystal microbalance
Fc	Ferrocene
GC	Glassy Carbon
IPA	Isopropyl alcohol
IR	Infrared
ITO	Indium tin oxide
I	Current
MB	Methylbenzene
MP	Methylphenyl
NB	Nitrobenzene
NP	Nitrophenyl
NiCr	Nichrome
PB	Phosphate Buffer
PDMS	Polydimethylsiloxane
rpm	Rotations per minute
SAM	Self assembled monolayer
SCE	Saturated calomel electrode
SEM	Scanning electron microscope
$[Bu_4N]BF_4$	Tetrabutyl ammonium fluoroborate
UV	Ultraviolet
υ	Scan rate
XPS	X-ray photoelectron spectroscopy

Chapter 1: Introduction

1.1. Applications of Surface Modification

Assembling thin layers of molecular species on surfaces enables the formation of chemically well defined surfaces and control of surface functionality. The aim of surface modification is to attach molecular species with specific functionality, in a controlled manner to surfaces. Surfaces such as these are found to be useful in a wide array of applications such as sensors,[1,2,3,4] molecular electronics,[5,6,7,8] biotechnology,[9,10,11] and corrosion inhibition.[12]

Surface modification in its simplest form, is designed to protect surfaces from harsh environmental conditions. For example, the galvanizing of various metals with zinc protects the metal underneath because the zinc reacts with air and water to form an impermeable layer, thus inhibiting corrosion of the metal underneath.[13] Current methods of corrosion inhibition that utilize excessive chromating and phosphating.Recent research by Pinson and coworkers has indicated that organic films, based on the reduction of aryldiazonium salts, can also act as corrosion inhibitors on iron.[12] This method provides a more environmentally friendly alternative to Films derived from diazonium salts on iron exhibit high corrosion inhibition efficiency.[12]

The use of modified surfaces in sensing systems for analytical and biochemical purposes is becoming increasingly popular. Covalently grafted organic films with suitable terminal

groups can act as sensors to enhance selectivity for analytes in solution. Molecules can be tethered for additional reactions at the interface. Devices for specific sensing purposes have been developed for detecting species such as dopamine, glucose oxidase (GOD), catecholamines, and nucleic acids.[1,2,4,9,10,11] For example, dopamine sensors have been fabricated by grafting 4-sulfobenzene to an electrode comprised of carbon fibers. These molecules allow for an increased sensitivity to dopamine due to the increased adsorption of molecules at the interface.[10] The attachment of oligonucleotides to surfaces with diazonium derived films has been achieved, which has potential applications for DNA testing.[1] Another example of sensing devices manufactured in this manner are GOD sensors. A carbon electrode is modified with a diazonium derived film, and functionality is used to obtain links to immobilize species in solution.[2]

Surface modification is an important aspect of molecular electronics. The creation of more efficient and faster computing devices entails the miniaturization of electronic components. As current computing devices are made smaller, problems arise, and new forms of component fabrication must be developed to achieve stable and functional devices. Patterning of surfaces with organic films functionalizes surfaces in a similar manner to electrochemical grafting, except modification only occurs in the regions where the modifier contacts the surface. Nanoscale structures created by patterning of the surface are useful for purposes such as data storage, and information processing. It is hoped that new technologies and applications can be developed from nanofabrication techniques.[14,15]

1.2. Gold and Self Assembled Monolayers

Gold has proven to be quite a popular surface to work with because of its many attractive properties. It is very easy to chemically modify or generate patterned gold interfaces, and in turn it is also easy to characterize those modified surfaces via the use of techniques such as surface plasmon resonance (SPR) or with the use of an electrochemical quartz crystal microbalance (EQCM).[17] Gold can be made optically transparent, which is very useful for spectroscopic reasons. It can also be used to fabricate a wide array of structures at a very small scale (micro- to nano-scale).

Thiols have proven to be popular species for coupling to gold as they spontaneously bind to the gold surface forming Self-Assembled Monolayers (SAMs).[18,19,20] The formation of SAMs entails simply placing the gold surface into a thiol containing solution. The thiols will gradually bind to the surface and over time will pack tightly and arrange themselves to minimize energy at the interface. They commonly adopt a tilt angle of 30 º; this depends on the chemical structure of the thiol. There are three main components to a SAM: firstly there is the Au-S bond that anchors the thiol to the surface; secondly there is the chain linker or main body of the molecule; and finally a functional head group which can be utilized for further coupling reactions. Well ordered SAMs form desirable structures over large domains of the surface.

Despite the advantages of grafting SAMs to gold, there are some serious limitations. The SAM is potentially unstable on prolonged contact with air or solution, resulting in desorption of the monolayer and the creation of defects and pinholes. This is accelerated

at elevated temperatures and in particular solvent conditions. There is also a limited potential range over which thiols will remained adsorbed to the surface.[2122,23] These disadvantages lead us to look for an alternative modification strategy. Films derived from diazonium salts have been observed at carbon surfaces[24,25,26] and exhibit strong and stable structures. This has also been reported at gold and other metal/metal oxide surfaces, although the nature of the interaction has not been fully investigated.

1.3. Surface Modification using Aryldiazonium Salts at Carbon

Aryldiazonium cations have the general structure X-Ar-N_2^+, where X is representative of a functional group.[27] The mechanism of formation of an aryl film at a carbon surface is through the reduction of aryldiazonium salts and is outlined below (Fig. 1).[12,28] Initially the diazonium salt is reduced at the electrode, with the elimination of N_2. A radical is formed which will attack the surface to generate a covalent bond.

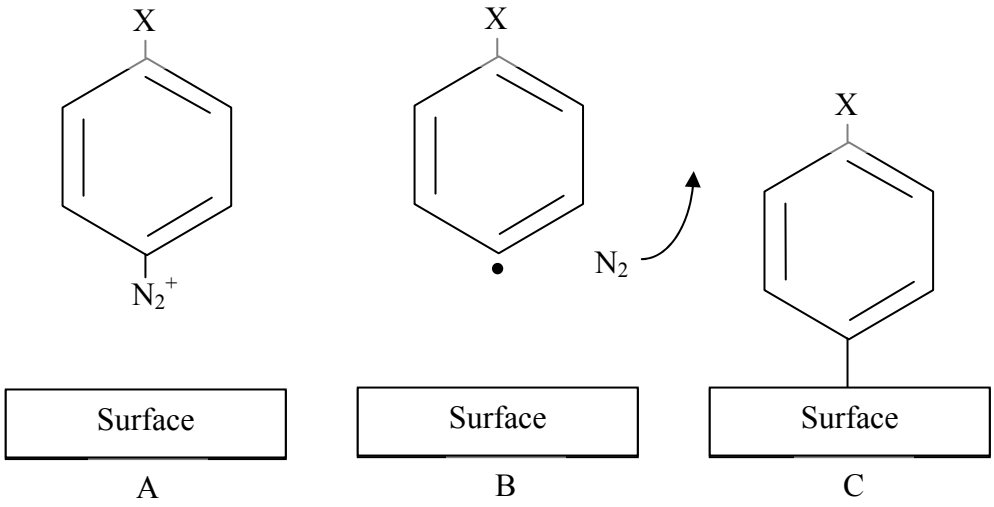

Figure 1: The mechanism for the formation of monolayer thick diazonium film. A diazonium molecule is reduced at the electrode surface (A), forming a radical and N_2 is eliminated (B). The radical then attacks the surface forming a covalent bond (C).

Multilayers are known to form whilst using diazonium salts to deposit films on carbon surfaces.[12,29,30,31] Multilayer formation occurs much the same as monolayer formation, except that the aryl radicals attack the freshly deposited film bound to the surface. The radical attack is favored at the para position on the benzene ring of an already bound molecule (Fig.2). This process enables thicker films to be formed, although the films will be disordered in nature.

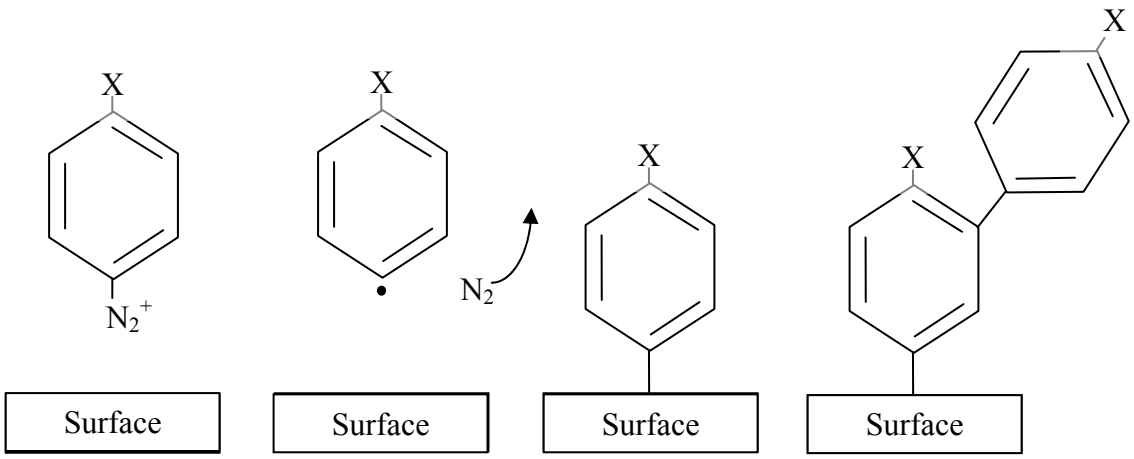

Figure 2: Mechanism of multilayer formation showing attack of nitrophenyl radicals at the para position of the already bound nitrophenyl moiety.

Factors that have been used to control the film coverage at the surface include diazonium salt concentration, deposition time and reduction potentials.[32] Throughout the literature describing surface modification using diazonium salts, there has been no standard method for modification. As diazonium salt concentration, and deposition time increase and reduction potential becomes more negative of the diazonium cation reduction peak, surface coverages are shown to increase. Film formation will effectively stop once the film is thick enough to stop electron transfer to species in solution.[32]

Films have been characterized with techniques such as electrochemical impedance spectroscopy (EIS), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), infra red (IR) and Raman spectroscopy.[33-37] Direct evidence for a C-C bond between the surface and modifier has not been conclusively obtained, however, the stability of the films is consistent with a strong covalent attachment. The structure and

stability of films derived from diazonium salts has been investigated in some detail. Unlike their thiol counterparts these films have a much larger potential window before desorption.[38] Films on carbon also show resilience towards sonication in a variety of solvents. It is suggested that weakly adsorbed or non covalently bound parts of the film are lost after sonication, leaving only the strong covalently bound molecules at the surface. This also implies that entrapment of unreacted diazonium molecules or electrolyte in the film has occurred.

The various properties exhibited by diazonium derived films on carbon, coupled with the attractive properties of gold surfaces, make the modification of gold surfaces via the reduction of aryldiazonium salts a desirable alternative to modification with SAMs.

1.4. Surface Modification using Aryldiazonium Salts at Metals and Metal Oxides

Reduction of aryldiazonium salts to grafted films is also observed at surfaces other than carbon, such as Si, Fe, Pt, Pd, ITO (indium tin oxide), Co, Ni, Zn, Cu, GaAs and Au.[36,39-44] The process by which these films are formed is thought to be the same as that at carbon, with the formation of monolayers and multilayers being observed.[17]

Electrochemical reduction of diazonium salts at iron surfaces forms a strongly bound film that is largely resistant to harsh sonication treatments in a variety of solvents. Films have been characterized using XPS, electrochemistry, IR spectroscopy and Rutherford backscattering measurements.[34,46] The observation of a covalent bond between surface

and modifier was seen at an iron surface.[46] However spectroscopic methods have not fully quantified a covalent bond between a gold surface and a diazonium derived film. There is some XPS evidence for a Au-C bond, but the data obtained is not conclusive.[17] Infrared spectroscopy also has failed to detect a Au-C bond, although the research has demonstrated the absence of a N ≡ N bond indicating that the diazonium salt has been reduced by the loss of N_2.[29,47]

There is strong evidence for diazonium film formation at gold, however the process is less understood than at other surfaces, largely because no direct evidence for a covalent bond between the gold surface and the phenyl modifier has been observed. Formation of diazonium films at a gold surface proceed initially to deposit a monolayer, followed by multilayer deposition. This was discerned through the use of an EQCM and multilayers were observed through AFM depth profiling.[17,29] In addition diazonium salts with different substituents were found to exhibit varying grafting efficiencies. Nitrophenyl films appear to graft more efficiently than other films such as those of the carboxybenzene diazonium salt. This may be because the nitrophenyl radicals that are formed in solution may react relatively more efficiently with the surface film rather than attacking other radicals or molecules in the modifier solution. Prolonged ultrasonication of the films in solvents yielded only a small percentage of film loss, which provides further evidence for a film bound firmly through covalent bonds.[17]

1.5. Spontaneous Reactions at Carbon and Metal Surfaces

Spontaneous reactions at surfaces are attractive, as they are relatively easy to achieve under controlled conditions such as time and temperature. Research at a variety of surfaces has revealed that spontaneous reactions occur between diazonium salts in solution and the surface, forming films. These surfaces include carbon, iron, silicon, copper, nickel and zinc.[16,46,48] Surfaces with spontaneously grafted films have been characterized with a number of different techniques, including XPS, EIS, AFM, cyclic voltammetry, IR and Raman spectroscopy. The films formed are stable to sonication and rinsing, which suggests they are covalently bound to the surface. No spontaneous reactions have been reported between gold surfaces and diazonium salts.

The spontaneous reaction between gold surfaces and thiols has been exploited in various soft lithographic techniques which can be used to fabricate micro- and nano-scale structures at surfaces. Microcontact printing has been most popular for the modification of gold surfaces with SAMs,[49,50] as complicated features down to nanometer scale have been assembled in short periods of time. This form of surface modification involves the use of polydimethylsiloxane (PDMS) stamps to transfer modifier to the surface. Where contacts are established, modifier can bind to the surface, and once removed, the surface will be functionalized in the patterned region.[14] The fabrication of surfaces via these methods is important for applications in molecular electronics and sensing devices as mentioned earlier in this chapter.

Despite the strong evidence for diazonium derived films spontaneously grafting to many metal surfaces, it has yet to be observed at gold. If films do spontaneously graft to gold surfaces, then patterning of the surface via microcontact printing should be achievable.

1.6. Aims

This project investigates films grafted to gold surfaces from the reduction of aryldiazonium salts. The specific aims of this project are to:

(1) Gain a better understanding of the gold-film interface by monitoring gold oxide electrochemistry at reconstructed gold surfaces in the presence and absence of films;

(2) Investigate the stability and structure of 2 different diazonium derived films through the use of redox probes, gold oxide electrochemistry and contact angle measurements;

(3) Obtain evidence for the spontaneous reaction between aryldiazonium salts and gold surfaces; and

(4) Explore the feasibility of patterning gold surfaces using microcontact printing.

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Chapter 2: Experimental

2.1. Surfaces and Electrodes

2.1.1. Cleaning and Preparation of Polycrystalline Gold Surfaces

Before any electrochemistry was carried out, the gold surface had to be clean and bare of surface deformations. To achieve this, the gold was subjected to various levels of polishing. The surface was first hand polished with sandpaper of progressively smaller grains. Next it was polished for 1 hr with 1 micron alumina and Milli-Q water on a piece of micro-fabric, before finally being polished with 0.05 micron alumina and Milli-Q water for 1 hr. Alumina polishing was done with a handheld vice. The surface was polished until there were no visible markings or scratches. The gold electrode was then thoroughly ultrasonicated alternately in water and acetone (for 10 min each), over the period of 1 hr, so as to rid the surface of any traces of alumina. Fresh solvent was used in each ultrasonication step to ensure the elimination of alumina. This procedure was used at approximately 3 month intervals, when the surface had visibly degraded.

Before a set of experiments was carried out at the gold surface, it underwent potential cycling for a prolonged period of time (2-4 hr). The aim of this is to arrange the gold atoms at the surface into a particular conformation as to optimize the reactivity of the surface[1, 2]. First the electrode was polished with a damp tissue, then flame annealed with a hydrogen flame, before being set up for cycling in an N_2 purged solution of 0.01 M

$HClO_4$ (20 min). Cycling was carried out between the range of -0.2 V to +1.45 V at a speed of 50 mVs^{-1}.

Later in the research an additional step was used for daily cleaning and preparation of the surface. Piranha treatment is a harsh cleaning process designed to remove any organic species from the surface of the electrode. Three parts of conc. H_2SO_4 to one part of H_2O_2 make a solution of piranha. All work is carried out in glass, and caution must be taken to not spill any as it is highly corrosive. The two components are mixed thoroughly before the gold surface is dipped into the solution for approximately one min. It is then removed, rinsed with Milli-Q water and acetone, air dried under N_2, before it is flame annealed with a H_2 flame and potential cycled.

When using the polycrystalline gold electrode, a meniscus had to be formed between the electrode surface and the solution in the cell (Fig.1). However, it can be noted that there is a specific orientation of the meniscus needed to obtain reliable results. The meniscus must be level with the surface of the electrode to achieve an adequate contact (A). If the meniscus is too small (B), it will not cover the surface of the working electrode, giving an irreproducible result. On the other hand if the meniscus forms up the sides of the electrode (C), data obtained from the extra area on the sides of the electrode will interfere with results.

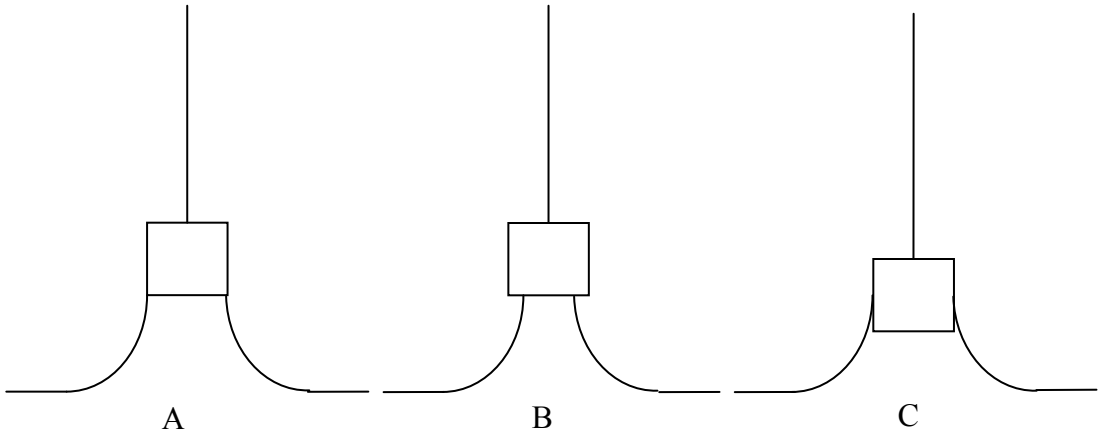


Figure 1: Figure showing the ideal meniscus formed between the polycrystalline gold electrode and the electrolyte solution (A), a meniscus that is too small (B) and a meniscus that is too large (C).

2.1.2. Preparation of Au/Si Electrode Surfaces

2.1.2.1. Preparation of Silicon

For a large part of this project surfaces of suitable dimensions were needed for use with particular analytical methods. Whilst the large polycrystalline electrode was useful for electrochemical analysis, it was too bulky for methods involving contact angle measurements or microscopic imaging. For these techniques special surfaces were fabricated from gold films deposited on silicon wafer.

N-type silicon (100) wafer was first coated with photoresist. The aim of this is to protect the silicon surface when it is scored and cut into small pieces. A spin coater was used to

coat the silicon wafer with SU1518 photoresist at a speed of 300 rps for approximately 1 min. The silicon wafer was then placed in a container wrapped in tin foil to avoid exposure to UV light. It was baked in an oven for 15 min at 120 ºC.

After the curing stage, the photoresist covered silicon was cut into 1 cm^2 sections with a diamond tipped cutter. The plate was first mounted onto the machine and secured in place with the use of a vacuum. Next the diamond tipped cutter was applied with pressure and the surface scored at 1 cm intervals in a grid pattern. After scoring, the wafer was broken into small square pieces along the scored lines. Any waste shards were discarded into a hazardous materials bin.

The next stage of preparation was the washing of silicon surfaces in various solvents to remove the photoresist. Ultrasonication in first methanol, then isopropyl alcohol, and finally acetone, for periods of 5 s each was used to remove the photoresist from the surface of the silicon. The pieces were then air dried under N_2 and stored ready for evaporation.

2.1.2.2. Evaporation

After the removal of the photoresist, the silicon pieces had gold evaporated onto their surface via the use of a Balzer's Evaporator. Titanium or NiCr was used as an adhesive layer between the gold and silicon to form a stable surface. Film thicknesses of 30 nm and 200 nm were used for titanium and gold respectively. This was achieved by

resistively heating the metal in a vacuum until the metal evaporates. The evaporated metals are deposited smoothly on the substrate surface, where the thickness can be controlled *in situ.* A quartz crystal inside the evaporator chamber was used to monitor the amount of metal deposited. Frequencies of 500 Hz and 16 KHz were used to achieve the desired coverage of Ti/NiCr and Au respectively. After evaporation the surfaces were stored in a dessicator under vacuum for no more than two weeks, so as to minimise any contamination.

2.2. Electrochemical Methods

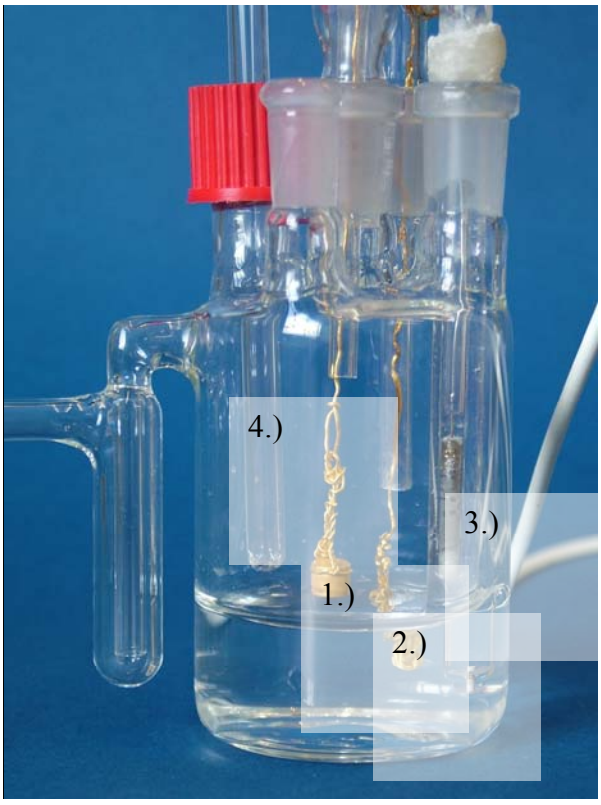
2.2.1. Instruments and Software

For all electrochemical measurements in this project, either a computer controlled EG&G PAR 273A potentiostat or a computer controlled EG&G PAR 362 potentiostat coupled with a powerlab/4sp was used.

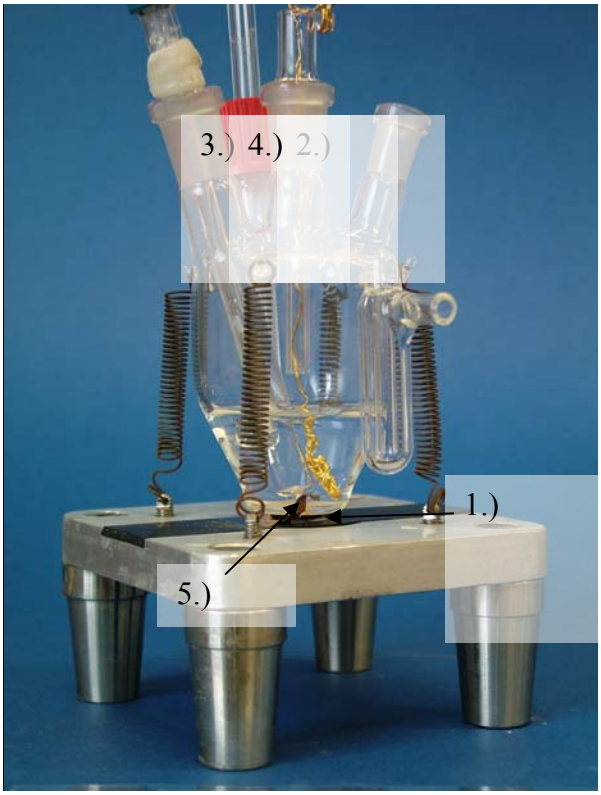
2.2.2. Cell Setup

All electrochemistry was carried out in one of two types of electrochemical cell (Fig.2). A standard 3 electrode cell was used for experiments with the polycrystalline bulk gold working electrode. When utilising the Au/Ti or Au/NiCr on silicon working electrodes, a different setup was required. The cell for such work has been detailed fully before[3]. The gold surface is positioned between a metal base plate and pear shaped glass cell with a

hole in the base. Viton O-rings between surface and cell, along with four metal springs attached to the four corners of the cell, stabilise the setup, and provide a seal to avoid leakage of solution. A strip of copper lies between the O-rings and the electrode, maintaining electrical contact with the gold surface. For each experiment an, auxiliary electrode and reference electrode was used in addition to the gold working electrode. Gold was used exclusively as the auxiliary in all work. In aqueous solutions a SCE was used as the reference electrode, whereas in non-aqueous solutions a silver wire pseudo reference electrode was used. The potential of the Fc/Fc^{+} couple was 0.37 V.



1.) Gold Working Electrode
2.) Gold Auxiliary Electrode
3.) Reference Electrode (SCE)
4.) Gas line



1.) Gold Working Electrode
2.) Gold Auxiliary Electrode
3.) Reference Electrode (SCE)
4.) Gas line
5.) Copper strip

Figure 2: Cell Setup for a standard 3 electrode cell (A) and a pear shaped 3 electrode cell with a hole in the base (B).

2.2.3. Synthesis and Solutions

Diazonium salts were synthesised using the following method[4]. A mixture of 2 ml of fluoroboric acid and 2 ml water is added slowly to 5 mmol of arylamine, with stirring and cooling. Next 5 mmol sodium nitrite dissolved in a small amount of water is added slowly to the solution with continued cooling and stirring. The crude product is left to precipitate with cooling, before it is collected under vaccuum and washed with small amounts of cold 5 % fluoroboric acid, methanol, and copious amounts of ether. It was then left overnight in the fumehood to air dry. The crude product was then recrystallised in cold acetonitrile (ACN) and washed with cold ether. Care was taken not to expose the

product to UV light, by encasing apparatus with aluminium foil. The product was then stored under vacuum in a dessicator.

The electrolyte used in all modification experiments was tetrabutylammonium tetrafluoroborate ($[Bu_4N]BF_4$), which was synthesised via the following method. First 40 ml $[Bu_4N]OH$ (40 %) diluted with 100 ml water, and 5 ml fluoroboric acid diluted with 25 ml water was mixed with stirring until a white precipitate formed. The precipitate was collected under vacuum and washed with water. To eliminate all traces of moisture from the electrolyte it was first left to air dry for 30 min, before being placed in an oven at 45 ºC overnight and finally it was placed in an oil bath at 80 ºC for 2 days under vacuum. Once the drying process had finished, the electrolyte was stored under vacuum in a dessicator.

Phosphate buffer (PB) solutions were made from 0.8533 g Na_2HPO_4 and 0.847 g $KHPO_4$ in 250 ml Milli-Q water, and the pH adjusted to approximately 7 using concentrated NaOH. All acid solutions were made from stock with different dilution factors to achieve the desired concentrations.

2.4. Modification with Diazonium Salt

The electrode was modified by reduction of the diazonium salt in a cell containing a gold working electrode, silver wire reference electrode, gold auxiliary electrode, 1 mM diazonium salt, and 0.1 M $[Bu_4N]BF_4$ in ACN. The ACN had been dried over CaH_2 for

several days, before being refluxed under nitrogen for 2 hrs and collected. It was then degassed with nitrogen for a further 20-30 min before modification was carried out. Cyclic voltammetry at a scan rate of 50 mVs^{-1} was used to determine the potential of the modification peak. A potential approximately 0.15 V negative of the peak was chosen for modification. This potential was applied for a set amount of time, depending on the nature of the experiment.

2.2.5. Aqueous Electrochemistry

Gold oxide reduction was analysed using cyclic voltammetry to obtain a plot of current *vs.* potential over the range of 0 to 1.45 V in a solution of 0.01 M $HClO_4$. The cell contained the gold working electrode, gold auxiliary electrode, SCE and a N_2 gas line used to purge the solution for 20 min prior to any scans. The voltammetric scan showed the formation of gold-oxide and the reduction of these oxides. This information was then in turn analysed with a curve fitting program, linkfit[5]. Data obtained from linkfit was used to calculate the charge associated with the gold oxide reduction.

Cyclic voltammetry of potassium ferricyanide was used to probe electron transfer at electrode surfaces. The cell contained 5 mmol $Fe(CN)_6^{3-}$, 0.1 M KCl, a PB at approximately pH = 7, gold working electrode, gold auxiliary electrode and a SCE reference electrode[6]. Cyclic voltammagrams were obtained between the range of 0.6 V and -0.2 V at a scan rate of 100 mVs^{-1}.

2.3. Soft Lithography

2.3.1. Preparation of the Silicon Master

A wafer of p-type silicon was cut into quarters approximately 5 cm x 5 cm with a diamond tipped cutting apparatus. Two hot plates were set up at a temperature of 110 ºC. Silicon wafer pieces were spin coated with SU8 photoresist. Two steps were needed for the spin coating. First the wafer was spun at 150 rpm for 15 s, and then at 3000 rpm for 20 s. After use, the spin coater was cleaned with the solvent, 'Remover pg'. The wafer pieces were then placed in small evaporating dishes.

The photoresist coated wafers had a circular pattern transferred to the surface using a chrome on gold mask and UV irradiation. Emelyn Tan (UoC) assisted with this procedure. After the wafers were taken out and put onto the hot plate for 10 min at 110 ºC. The wafer is then developed in a glass dish for 10 min with 1-methoxy-2-propyl-acetate, followed by rinsing with acetone and IPA. Next the silicon wafers were placed in an oven at 95 ºC for 20 min.

2.3.2. Preparation of Polydimethylsiloxane (PDMS)

The PDMS elastomer was prepared in a small plastic container. Ten parts of sylgard 184 base to one part of hardener was used. This solution was mixed thoroughly and left for

approximately 1 hr in a fumehood. The purpose of this was to allow air bubbles within the elastomer to escape, giving a uniform texture.

Next the silicon masters were placed into a small plastic dish and coated with the PDMS solution. Any air bubbles trapped in the elastomer were gently removed by touching with a plastic pipette. Finally the PDMS coated wafer was placed in an oven at 95 ºC for 20 min. The PDMS stamps were then able to be peeled off the master and prepared for extraction.

2.3.3. Extraction

The extraction process involves soaking the PDMS stamps in different solvents over several days.[7] First the stamp is soaked in pentane for 2 days, then toluene for 1 day, ethyl-acetate for 1 day, acetone for 1 day and finally it is dried in an oven at 120 ºC for 2 days. The purpose of the extraction is to remove as much of the unreacted PDMS monomer as possible and hence to minimise contamination of printed surfaces by PDMS residues.

2.3.4. Printing

The practical part of soft lithography involves stamping of PDMS inked with the reactive species onto the surface for a selected amount of time. A solution of 20 mM diazonium salt in DMF or ACN was used for the inking process. The PDMS was cut into small

pieces able to cover the surface of the electrode thus maximising coverage. It was then plasma treated with a plasma asher for 30 s at 500 W. The aim of plasma treatment was to improve the hydrophilicity of the surface (as PDMS is very hydrophobic), so that the PDMS can be easily inked for stamping (Fig.3).[7,8] All stamping was carried out within 1 hr of the plasma treatment so as to avoid loss of hydrophilicity.

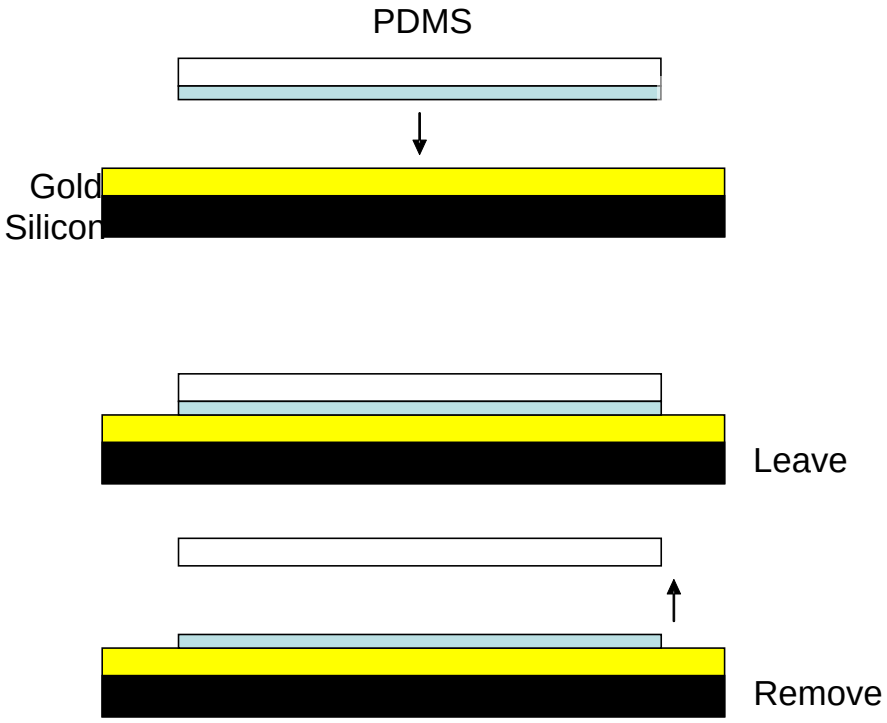


Figure 3: Basic outline of the printing process. A PDMS stamp coated in modifier is printed onto the substrate and removed after a selected time, leaving a modified surface

The PDMS is inked by placing it face down into the solvent/diazonium salt solution for 1 min. In the standard method for printing the stamp is removed and dried under nitrogen till it appears dry. It is then left for 30 s in air to dry, before being stamped onto the surface. The stamp was left for a desired time period before being removed. After removal of the PDMS stamp, the gold surfaces were first ultrasonicated in acetone for 20

s to remove any unreacted modifier from the surface, before a final ultrasonication in IPA for 10 s to remove solvent drying marks. The gold surfaces were then dried under nitrogen and stored in a plastic container in a dessicator under vaccum.

2.4. Contact Angle Measurements

Water contact angle measurements were taken on bare and modified gold surfaces. The gold surface was positioned on a stage, a 2 μL drop of Milli-Q water was placed onto the surface using a micro-syringe, and two images were captured using the Video (for Windows NT) software. After an image of the drop had been obtained 3 contact angle measurements were taken at each side of the drop. The surface is then removed and rinsed with Milli-Q water before being air dried with nitrogen. This process is repeated for a second drop. This gives 24 measurements for a single surface, which give an overall view of the surface's hydrophilicity.

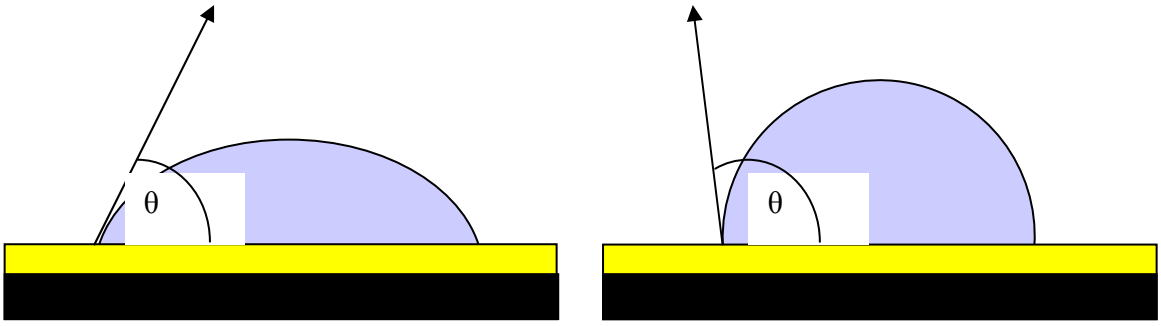


Figure 4: Examples of different water contact angles on a substrate. The greater the contact angle the more hydrophobic the surface.

2.5. SEM Measurements

SEM measurements were made using a Raith 150 e-beam lithography system, operating with the accelerating voltage at 10 kV, aperture at 20 and I filament of 2.39. The aperture and stigmation were carefully altered to focus the images prior to capture. Optimisation of the images was carried out by adjusting the brightness and contrast. Sam Yu (UoC) assisted with the operation of the Raith 150 e-beam.

2.6. Chemicals

Chemical	**Formula**	**Supplier**
Sulphuric Acid	H_2SO_4	BDH
Nitric Acid	HNO_3	BDH
Perchloric Acid	$HClO_4$	BDH
Hydrochloric Acid	HCl	Riedel-de Haen Ag Seelze-Hannover
Fluoroboric Acid	HBF_4	BDH
Pottasium Chloride	KCl	BDH
Sodium Pechlorate Monohydrate	$NaClO_4.H_2O$	Scharlau
Sodium Nitrite	$NaNO_2$	BDH
p-amino benzoic acid	$C_7H_7O_2N$	J T Baker
p-toluidine	C_7H_9N	Riedel-de Haen Ag Seelze-Hannover
p-nitroaniline	$C_6H_6N_2O_2$	Aldrich
Potasium Hydroxide	KOH	Scharlau
Potasium dihydrogen Orthophosphate	KH_2PO_4	BDH
Sodium Hydrogen Orthophosphate	Na_2HPO_4	Fisons
Sodium Hydroxide	NaOH	Scharlau
Potasium Ferricyanide	$K_2(Fe)(CN)_6$	Riedel-de Haen Ag Seelze-Hannover
Ethanol	C_2H_6O	BDH

Methanol	CH_4O	BDH
Ether	$C_4H_{10}O$	Commercial Solvent
Pet Ether	C_6H_6	Commercial Solvent
N-N Dimethylformamide	C_3H_7NO	BDH
Hydrogen Peroxide (40%)	H_2O_2	Wilsons Chemical Ltd
Acetonitrile	C_2H_3N	BDH
Tetrabutyl ammonium hydroxide	$C_{16}H_{37}NO$	BDH

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7) Lee, J.N. Park, C. Whitesides, G.M. *Anal. Chem.* **2003**, 75, 6544-6554

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Chapter 3: Gold Surfaces

3.1. Introduction

Metal surfaces are commonly used in the process of surface modification. Gold has proven to be popular due to its attractive properties, such as its ability to be easily chemically modified and patterned, and the wide array of spectroscopic methods that can be employed to characterise the surface, such as Surface Plasmon Resonance (SPR) or with the use of an Electrochemical Quartz Crystal Microbalance (EQCM). Gold surfaces used for electrochemistry consist of faces that are either comprised of a single crystal, or are polycrystalline in nature.

Single crystal faces have well defined surfaces with few defects such as dislocations, pits or steps. Metals will form a face centred cubic (FCC) crystal structure that can be cut to expose different crystal faces or index planes. The arrangement of atoms at the surface of the low index faces, (100), (110) and (111) are shown below (Fig. 1). Low index faces are commonly used as electrodes as they are much more stable then higher index faces and can be polished to give very smooth and uniform surfaces[1]. However, there is a limit to how large a smooth surface can be, no matter how carefully prepared. With areas greater than a few square micrometers, defects arising from grain boundaries, depressions, dislocations, pits or steps may be observed.

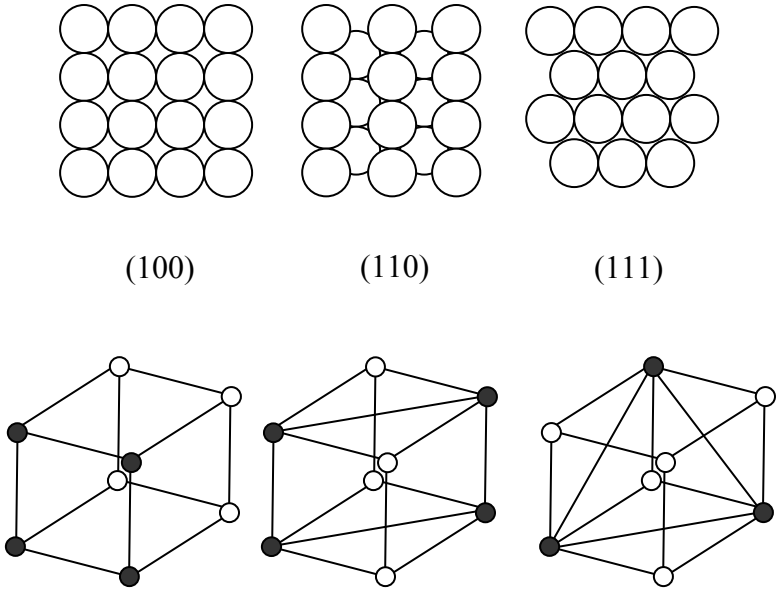

Figure 1: The low index faces of gold surfaces, (100), (110) and (111), showing the arrangement of atoms at the surface, and the atomic structure of a FCC crystal obtained from cutting along the planes (shown by closed circles). Adapted from reference 1.

When a metal is cleaved the atoms that are then exposed at the surface are no longer subjected to the same bonding forces. This leads to a change in the arrangement of the atoms so as to minimise surface energy. Reconstruction of the surface occurs during potential cycling. For example, if a gold surface of low index face (100) is flame annealed, the atoms will rearrange to form a surface more closely resembling the (111) index face. If this surface is placed into 0.01 M $HClO_4$ it will retain its new structure. However if it is cycled to increasingly positive potentials of around 1.45 V *vs* SCE, then the surface will undergo reconstruction. Past research with well defined single crystal

electrodes has shown that the properties of solid electrode surfaces depend strongly on the index plane presented to solution.[2]

Polycrystalline gold surfaces are comprised of a variety of regions that have different crystal structures. Each region will exhibit different electrochemical properties, so that the behaviour of a polycrystalline electrode will be a representative average of this. For example, a polycrystalline gold electrode may exhibit a mixture of low and high index planes at the surface. Each region has its own properties, but electrochemical analysis will provide an overall view of the electrode's surface structure as a whole.

This chapter discusses the voltammetry of a well constructed polycrystalline gold surface and the methods used to prepare electrodes before use. The effects of various treatments are then examined by observing the gold oxide reduction process. The purpose of these studies was to understand how the gold surface behaves during the film grafting experiments described in later chapters.

3.2. Results and Discussion

3.2.1. The Oxidation of Gold Surfaces

Most metal surfaces undergo oxidation upon exposure to air. However metals such as gold are relatively inert and will not oxidise under these conditions. It had always been

assumed that electrochemical oxidation of the gold surface doesn't take place and that oxide was formed through the anodic oxidation of water at the gold surface:

$$(1) \qquad Au + H_2O \rightarrow Au(O) + 2H^+ + 2e^-$$

However XPS studies have shown that anodic oxidation of the gold surface does occur, forming $Au(OH)_3$:[3]

$$(2) \qquad Au.H_2O + 2H_2O \leftrightarrow (Au(OH)_3)_s + 3H^+ + 3e^-$$

The reduction of the formed oxide can be seen as:

$$(3) \qquad Au(OH)_{3s} + 3e^- \rightarrow Au_s + 3OH^-$$

Applying an increasingly positive potential to the gold surface leads to the formation of a monolayer of gold oxide in the region of 1.3 - 1.5 V *vs.* SCE. As the potential is cycled back to 0 V the oxide is reduced around 0.7 - 0.8 V. Cyclic voltammagrams in deaerated 0.01 M $HClO_4$ (Fig. 2), give information on the different processes occurring at the gold surface. Regions A and B relate to the electrochemical oxidation and reduction of the gold surface[4,5]. The formation of a monolayer of gold oxide is limited by the amount of material that can be deposited at a surface. The area under the peak obtained from the reduction of gold oxide (region B) is used to determine the amount of gold oxide at the surface. In region C the current observed is associated with charging of the double layer

capacitance. From an enlarged view of this area the positive and negative current/potential traces should mirror each other. If this is not the case then slow potential induced structural changes are occurring. This is the process of reconstruction.[6,7]

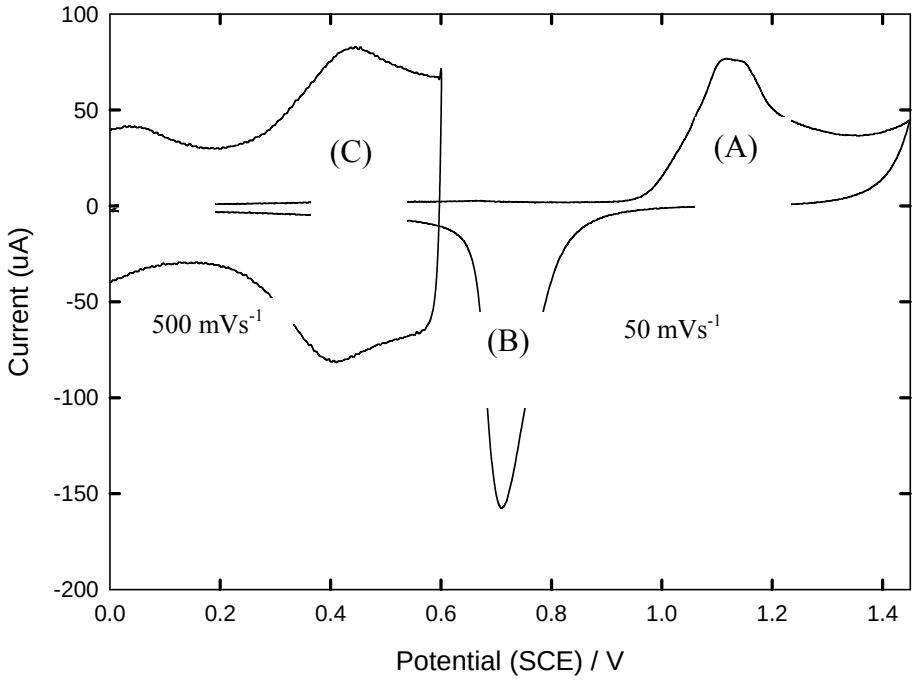

Figure 2: Voltammetric scans in 0.01 M $HClO_4$, showing the formation of gold oxides (A), their subsequent reduction (B), and the region of double layer charging(C).

In this work the amount of gold oxide formed at the electrode surface was determined from cyclic voltammetry using the curve fitting program Linkfit.[8] Linkfit gives the area under the gold oxide reduction peak. From the associated charge the surface area can be calculated as shown below.

$$Q_{ox} = (i \times E)/ \upsilon$$

$$A_{ox} = Q_{ox} / 400\ \mu C\ cm^{-2}$$

Q_{ox}, the charge associated with the reduction of gold oxide at a surface is determined by the area under the reduction peak divided by the scan rate. $A_{ox,}$ the area of gold oxide formed, is then obtained by dividing Q_{ox} by the charge required to reduce a monolayer of gold oxide at a polycrystalline surface, which is 400 μC cm^{-2}. The value of 400 μC cm^{-2} was chosen as an average value from several different values obtained from the literature.[2,9,10] The resulting figure is the area in cm^2 of gold oxide formed at the surface, which in this work was determined to be 1.5 times the calculated geometric area of the surface. This factor arises from various aspects of surface roughness, because the topography at the atomic level is relatively uneven, which is not taken into account when calculating the geometric area. A factor of 1.5 is considered a well prepared gold surface.

3.2.2. Cleaning and Preparation of the Gold Surface

Prior to each experiment, the polycrystalline gold electrode was prepared as described in chapter 2, to obtain a relatively smooth surface free of significant defects. Polishing with fine grained sandpaper removes the macroscopic defects, whilst polishing with finer grained alumina on microcloth creates a smoother surface, largely free of scratches and defects. Care must be taken to remove all traces of alumina before potential cycling, as alumina left on the surface can become strongly bound to the surface, interfering with results obtained from subsequent experiments.

After polishing, the surface will not be uniformly smooth, and minor defects and depressions will still be present. Flame annealing with hydrogen was used to relieve

stress on the atoms at the surface. Potential cycling in 0.01 M $HClO_4$ after the flame annealing reconstructs the interface to an unchanging steady state condition. This state of the gold surface was achieved prior to each experiment involving the polycrystalline surface.

A second cleaning method was introduced for the purpose of removing modifier. Piranha treatment involves immersing the electrode into a 3:1 solution of H_2SO_4 to H_2O_2. This solution is highly corrosive and is designed to remove all organics from the surface of the electrode, with little effect on the gold surface itself. As it is highly corrosive, safety precautions must be taken whilst working with it and electrode surfaces must be thoroughly rinsed before further cleaning stages. Piranha treatment was used as an additional step prior to flame annealing and potential cycling in 0.01 M $HClO_4$.

3.2.3 Factors Influencing Gold Oxidation

Factors such as the electrolyte identity, concentration and pH, temperature and the anodic polarization time[9] can influence the outcome of the cyclic voltammetric analysis. The following sections describe the effects of selected surface treatments on the gold oxide formation and reduction.

Acid is the usual medium for electrochemical reconstruction and is used in this work. When working in acidic media, the proton concentration of the solution will be high. Therefore protons generated from the oxidation of the gold surface (Eq.2) should not effect the pH of the solution near the electrode surface and there will be no changes noted

in the oxidation and reduction regions ((A) and (B) in Fig. 2). However if a neutral or basic solution is used to observe the formation of the gold oxide, then the protons involved in the redox reaction will cause an decrease in pH, thus causing shifts in the current in the aforementioned regions. It is possible to limit this effect in neutral and basic solutions by stirring of the solution to stabilise the pH.

$HClO_4$ and H_2SO_4 are commonly used as the media for electrochemical reconstruction of gold.[4,5] $HClO_4$ is chosen as the electrolyte for reconstruction in this work because the perchlorate anion does not adsorb to the surface as strongly as the sulfate anion.[4,5] The adsorption of sulfate ions leads to changes in the form of voltammetric scans obtained of the gold surface.

Different concentrations of electrolyte have an effect on how gold oxides behave. Voltammetric scans in 0.01 M $HClO_4$ and 0.1 M $HClO_4$ of a bare gold surface that has been reconstructed in 0.01 M $HClO_4$ are shown in Fig. 3.

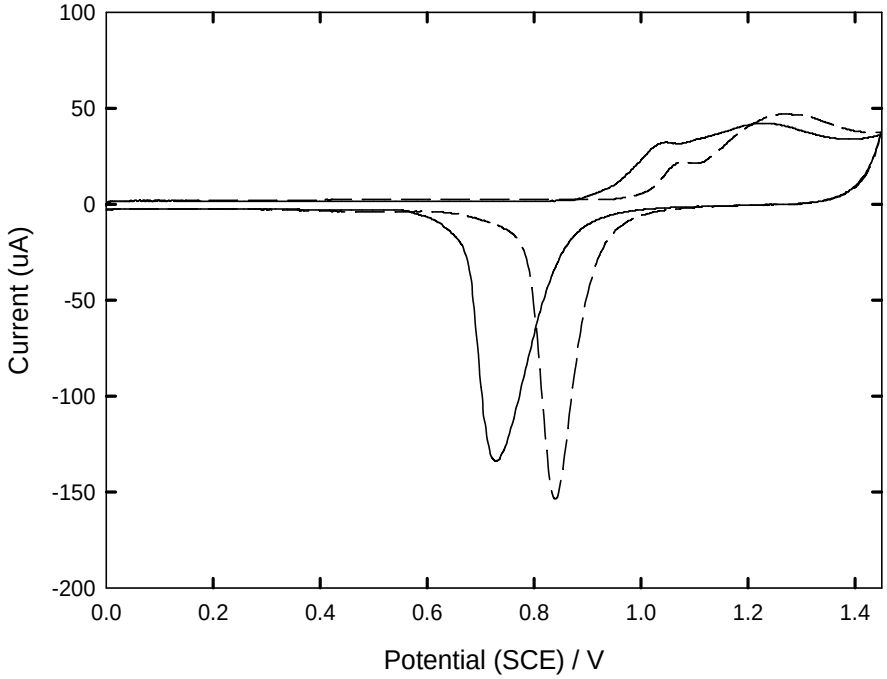

Figure 3: Voltammetric scans at scan rate = 100 mVs^{-1}, showing the effects on gold oxide formation and reduction in different concentrations of $HClO_4$. The solid line is a voltammetric scan taken in 0.01 M $HClO_4$, and the dashed line is a voltammetric scan taken in 0.1 M $HClO_4$. The electrode was first reconstructed in 0.01 M $HClO_4$.

The upper potential limit used for reconstruction of the gold surface is 1.45 V. If the potential is shifted to either a more positive, or a more negative value than 1.45 V then a change in the state of the gold oxide can be observed (Fig. 4). When the potential is scanned to a less positive value, less oxide is formed as noted through the decrease in the size of the reduction peak. However, as the potential is scanned further positive of 1.45 V, the reduction peak increases in size. Beyond 1.45 V the oxidation current increases steadily and is attributed to dissolution of gold atoms from the surface. The potential of 1.45 V was chosen as the upper limit for reconstruction because it gives maximum oxide formation without dissolution. Note, the particular gold electrode used for this experiment gave an abnormally large oxidation peak. It likely arises from a large defect area on the surface of the electrode that is exposed to oxidation, such as a pit or depression.

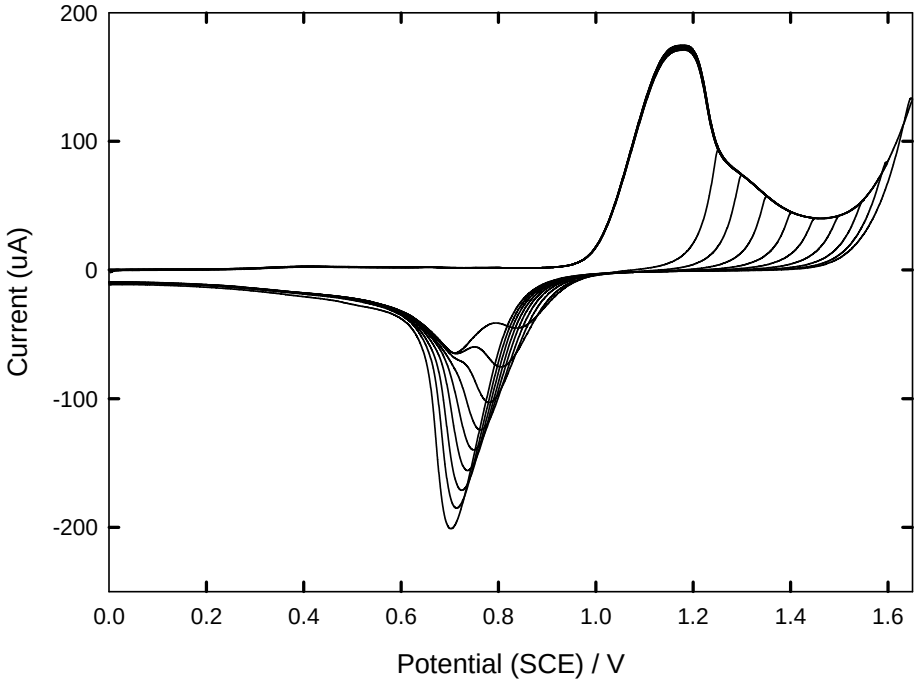

Figure 4: Voltammetric scans in 0.01 M $HClO_4$, scan rate = 100 mVs^{-1} scans showing the effect of scanning to different potentials on the amount of gold oxide formed.

3.2.4. Steady States and Treatment Effects

Gold surfaces may undergo spontaneous reconstruction if left at open circuit potential (OCP) in solution. Subjecting the gold surface to different environmental conditions will have varying effects on the steady state of the gold oxide. A study was carried out in which the polycrystalline gold surface was subjected to several different conditions for certain time periods. The aim of this was to observe how these different treatments would effect formation of gold oxides at the surface.

For each experiment the gold surface was prepared as described earlier in the work. Voltammetric scans (Fig.5) after various treatments show that leaving the reconstructed

electrode overnight in 1 M $HClO_4$ preserves the surface structure to a greater extent than when it is immersed in water for the same period of time. For a surface left overnight in 1 M $HClO_4$, the technique of flame annealing[11] causes an increase in the amount of oxide formed at the surface partly returning it to its initial state. Energy from the flame annealing excites the atoms at the surface into arranging into a more preferred conformation. Finally it can be seen that potential cycling for 3 hrs has the greatest effect on increasing the amount of gold oxide formation at the surface, and gives a state which is the same as the initial reconstructed surface. The cycling has continued what the flame annealing partly achieved, by slowly changing the conformation of the atoms at the surface to a more uniform and smooth state. Over time the oxide and corresponding reduction peak increases in area with slow potential cycling at 50 mV s^{-1}. A limit is reached after several hrs, where the peaks become stable with no further change. This state was chosen as the starting steady state for all further experiments.

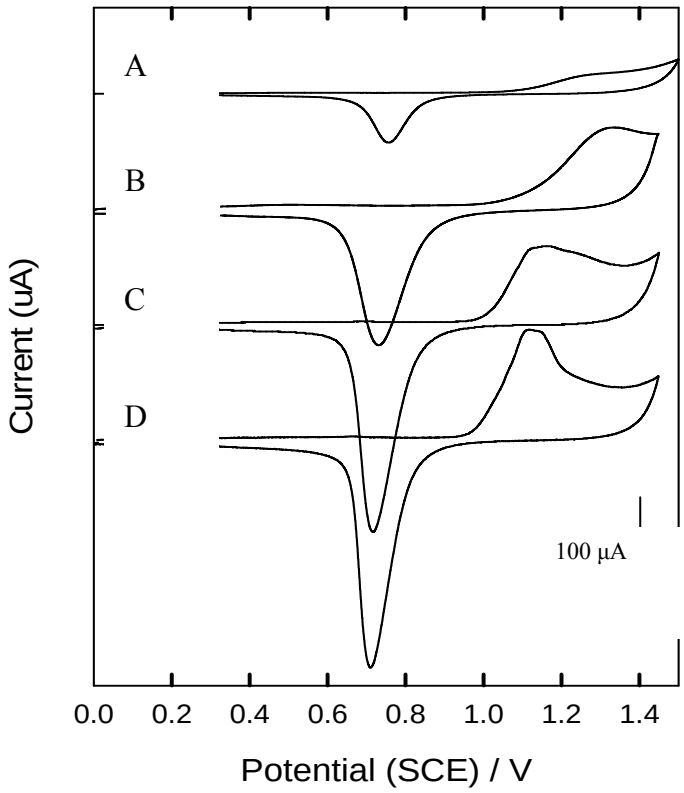

Figure 5: Voltammetric scans in 0.01 M $HClO_4$, scan rate = 100 mVs^{-1}, showing gold oxide formation at a polycrystalline surface: (A) left overnight in water, (B) left overnight in 1 M $HClO_4$, (C) left overnight in 1 M $HClO_4$ and then flame annealed, and (D) surface shown in (C) subjected to potential cycling for 3 hr.

The greater changes seen after leaving the gold electrode overnight in water as opposed to perchloric acid may be due to the ionic nature of the solution. Research has shown that anions such as iodide may bind to gold causing loss of mobility at the surface.[12] The iodide adsorbs to gold and the interaction between the iodide and gold causes the structure to remain stable with respect to time. Milli-Q water has very few ions present in solution. This would explain the large decrease in the oxide and reduction peaks as the atoms at the surface are more mobile with fewer anions to stabilise the surface. The gold surface that has been immersed in 1 M $HClO_4$ shows only a slight decrease in the

oxidation and reduction peaks and assuming a similar mechanism as proposed for iodide, it is suggested that ClO_4^- anions adsorb to the surface, forming a lattice that helps stabilise the gold atoms, leaving them with very little mobility. This would explain the relatively small decrease in the oxidation and reduction peaks.

The changes in gold oxide reduction charge were quantified for certain treatments. Gold oxide reduction was observed before and after: immersion in Milli-Q water overnight, being held at a set potential for 1 hr in 0.01 M $HClO_4$, left at a floating potential for 1 hr in 0.01 M $HClO_4$, and left exposed to the atmosphere for 1 hr.

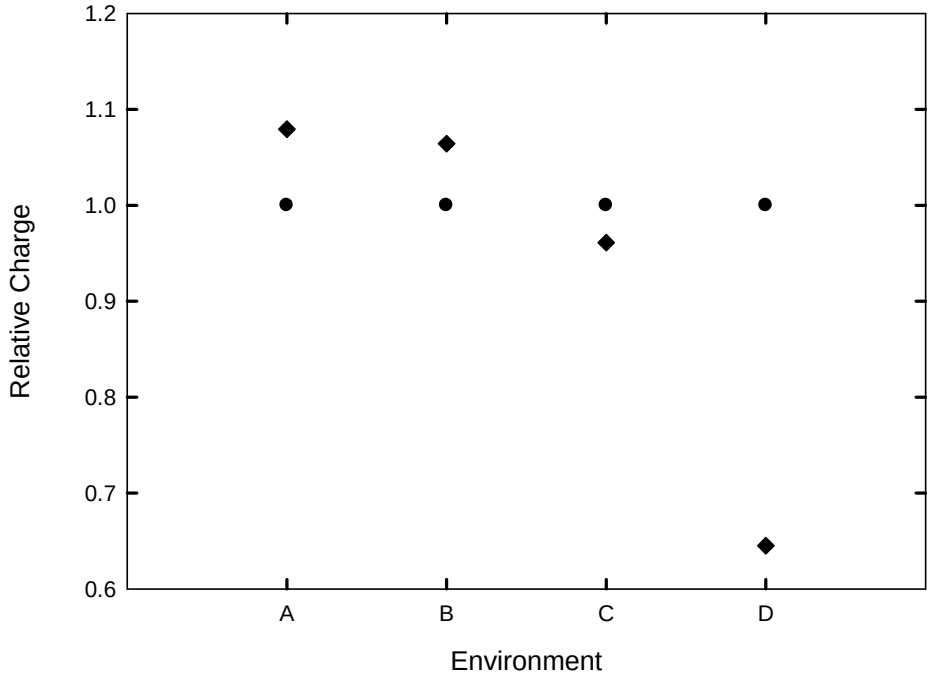

Figure 6: Plot showing the relative amounts of gold oxide formed at the surface before and after the reconstructed electrode has been subjected to various conditions. The different environments are: (A) held at -0.2 V for 1 hr in 0.01 M $HClO_4$, (B) held at a floating potential for 1 hr in 0.01 M $HClO_4$, (C) left in air for 1 hr, and (D) left overnight in water. Measurements of the charge at each surface were taken before (circle) and after (diamond) each treatment.

Fig. 6 shows the relative charge for reduction of gold oxide before and after each treatment. The relative charge before each treatment is 1. It can be seen (Fig.6), that leaving the electrode at an OCP for 1 hr or holding the electrode at a set potential of -0.2 V for 1 hr in 0.01 M $HClO_4$ leads to a very small amount of reconstruction of the surface. On the other hand, if the surface is left exposed to the atmosphere for an hr, there is a small decrease in the oxidation and reduction peaks. This is probably due to species in the air adsorbing to the surface and interfering with the oxidation of the surface, leading to a smaller charge. By far the greatest effect on the state of the gold oxide was caused by leaving it overnight in water. The amount of gold oxide subsequently being formed dramatically decreased.

3.2.5 Sonication

In most electrochemical research sonication is used to clean surfaces of physically adsorbed species. Sonication can involve the use of a variety of solvents and is a very energetic process. It is assumed that these factors would have an impact on the behaviour of gold oxide formation and reduction. Experiments were designed to observe the effects of sonication in different solvents on gold oxide formation/reduction.

A gold surface was cleaned and prepared with piranha solution, flame annealing, potential cycling for 3 hrs, and a voltammetric scan of the bare gold was obtained in 0.01 M $HClO_4$. The gold electrode was then immersed in acetonitrile, petroleum ether or

Milli-Q water for sonication, as these were the solvents that were commonly used to clean modified surfaces in later experiments.

Long periods of sonication increase the temperature of the water bath significantly. This in turn may lead to undesirable results as the fluctuating temperature will have a kinetic effect on the experiment. It is known that temperature has an effect on the rates of electrochemical reactions taking place in the different regions observed in voltammetric scans.[9] The temperature was maintained at either 45 ºC or 0 ºC during the experiments.

Sonication was carried out for time periods of 5, 10, 20, 40, or 60 min, after which the electrode was removed from the solvent and dried with nitrogen. A voltammetric scan of the gold oxides was then obtained in 0.01 M $HClO_4$ and the electrode returned to the solvent for further sonication (Fig.7). The relative charge is the charge associated with the reduction of gold oxides after sonication relative to the change for the reconstructed electrode before sonication.

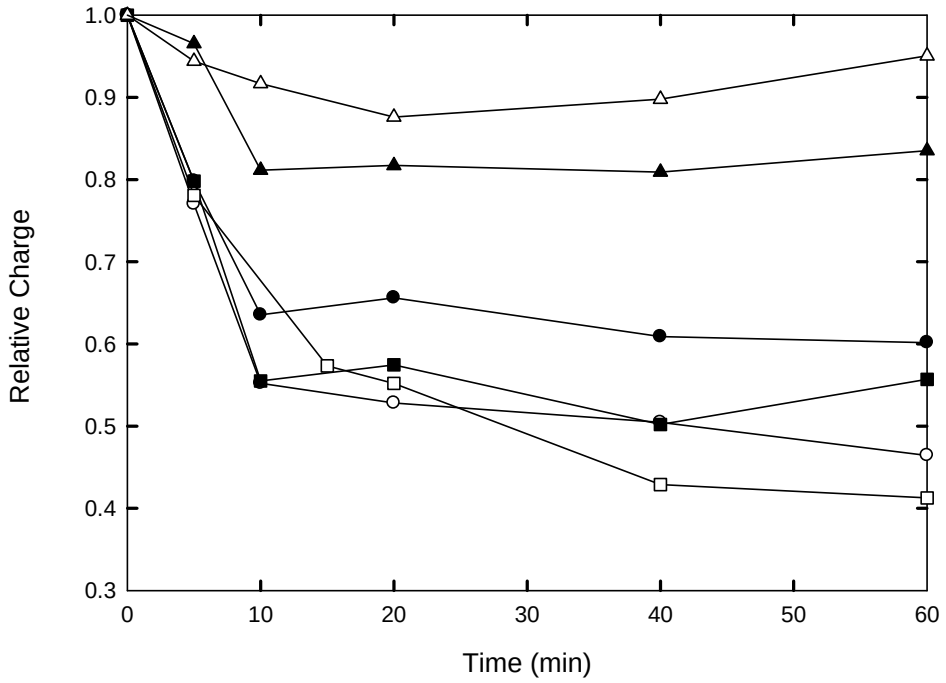

Figure 7: The effect of sonication on gold oxides in ACN (▲), PE (●), and Milli-Q water (■). Each experiment was carried out at 45 ºC (closed symbols) and 0 ºC (open symbols).

Sonication in ACN has little effect on the gold oxide, whereas in pet ether and water there are significant changes. For ACN, relative charge decreases by 10-20 %, whilst in PE and water the decrease is greater, being 40-60%. The larger decrease in the oxide reduction after sonication in PE and water could mean that the gold atoms at the surface experience a greater mobility in these solvents. Varying the temperature had no notable effect on the overall outcome of the experiments.

3.3. Conclusions

These investigations into the electrochemical reconstruction of gold establish that considerable effort is required to obtain a reproducibly stable surface. Subsequent treatment of the electrode changes the surface. Gold surface atoms are very mobile and their mobility appears to depend on conditions they are subjected to such as sonication. Solvents and anions can be seen to have different effects on the mobility of the atoms at the surface. Some may preserve the structure of the surface, whilst others degrade it. The structure of gold surfaces is ever changing and the difficulty in obtaining a steady state for surface characterisation may lead to difficulties in research relying on the measurement of the oxidation and reduction of a gold surface.

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Chapter 4: The Electrochemical Modification of Gold Surfaces with Aryldiazonium Salts.

4.1. Introduction

As mentioned in the introduction chapter the modification of surfaces provides functionalised interfaces that may be used for a wide variety of applications.[1,2] Surface modification of gold is common, as the surface has many attractive properties and is easy to characterise. This is especially so in the case of forming SAMs of thiols on the gold surface, which readily graft to the surface, and are easy to study. However SAMs are relatively unstable and other alternatives are sought.[3,4]

Films derived from diazonium salts have been shown to graft a variety of surfaces including gold. These films show a greater stability than those comprised of thiols.[3] However, the nature of the interaction between gold surfaces and diazonium derived films is not fully understood. It is suggested that a Au-C covalent bond is responsible for the strongly adhered film, as a covalent bond has been observed at other metal surfaces such as Fe.[5]

This chapter investigates the electrochemical grafting of diazonium salts to form films at gold surfaces. Methylphenyl and carboxyphenyl films are grafted to gold, and characterised with redox probes, cyclic voltammetry of gold oxides and contact angle measurements. A small amount of work is carried out with nitrobenzene diazonium for

comparison purposes. Modified surfaces are subjected to various treatments, and the stability and structure of the films are examined.

4.2. Results and Discussion

4.2.1 Diazonium Modification

Electrochemical reduction of a diazonium salt was used to modify the gold surfaces. The gold surface was prepared as described in the experimental chapter. A voltammetric scan between 0.2 and -0.4 V was initially done to find the modification peak, then the potential is stepped 0.15 V negative of this peak and held for a known time.[6] Films were grafted using electrolysis times of 1 min and 5 min. Plots of film thickness against grafting time obtained at carbon surfaces indicate that grafting times of around 5 min yield a complete modification of the surface.[7,8] Grafting times substantially less than 5 min appear to give a film that is porous in nature.

Three diazonium salts were primarily used in this study, the nitrobenzene, methylbenzene, and carboxybenzene diazonium salts, giving the nitrophenyl (NP), methylphenyl (MP), and carboxyphenyl (CP) film respectively (Fig.1-3).

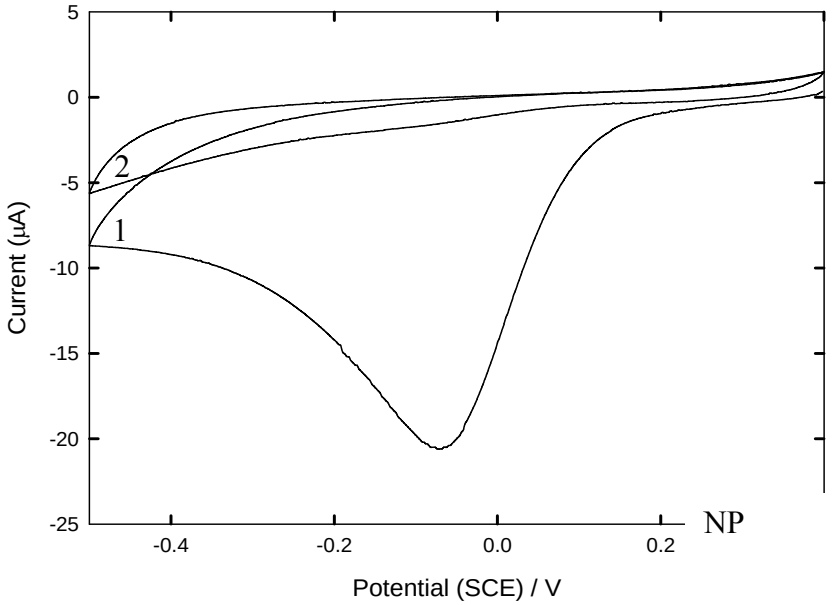

Figure 1: Voltammetric scans in ACN, 0.1 M $TBABF_4$, 1 mM diazonium and scan rate = 100 mVs^{-1}, showing modification of a gold surface with nitrophenyl groups.

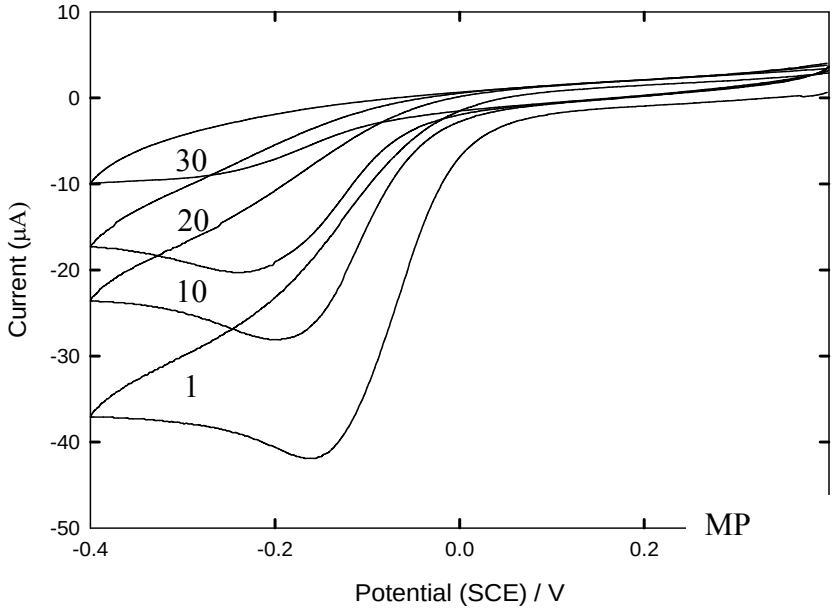

Figure 2: Voltammetric scans in ACN, 0.1 M $TBABF_4$, 1 mM diazonium and scan rate = 100 mVs^{-1}, showing modification of a gold surface with methylphenyl groups.

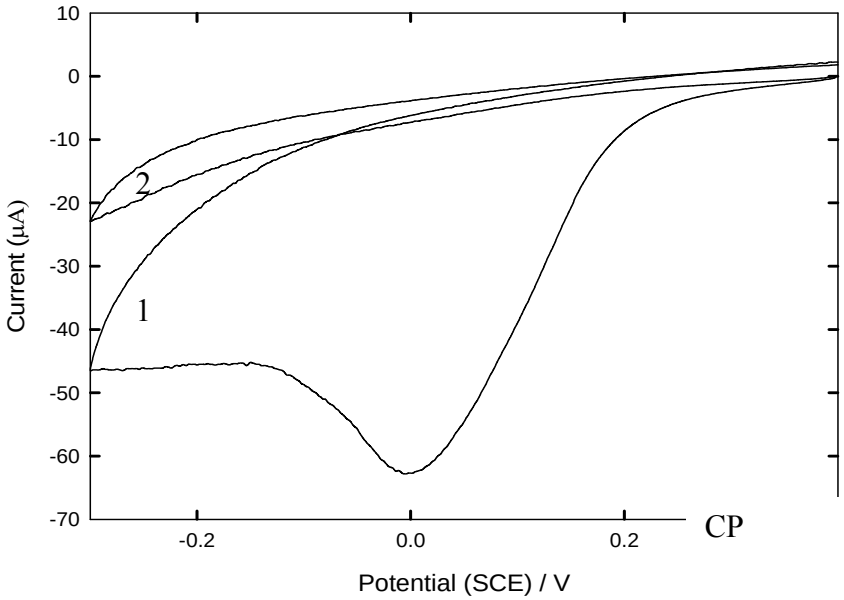

Figure 3: Voltammetric scans in ACN, 0.1 M $TBABF_4$, 1 mM diazonium and scan rate = 100 mVs^{-1}, showing modification of a gold surface with carboxyphenyl groups.

The first scan in each case shows the reduction of the diazonium salt. For the nitrophenyl and carboxyphenyl films the second scan shows no reduction peak. This is an indication that surface modification with a blocking film has occurred and is largely complete. However the methylphenyl film does not exhibit this behaviour, as a reduction peak is observed in each subsequent scan up to about the 30^{th} scan. It appears that formation of a blocking film is slower with this diazonium salt.

4.2.2. Effect of Negative Potentials on Surfaces and Grafted Films

Observing gold oxide formation and reduction at bare and modified surfaces gives information on the properties of the gold surface. The amount of gold atoms available for grafting can be determined. At a bare surface after pre-treatment conditions, as described in chapter 2, a large gold oxide reduction peak is observed. However at a modified surface the reduction peak is significantly reduced, indicating that a diazonium film has grafted to the gold, inhibiting the formation of gold oxide (Fig.4).[9]

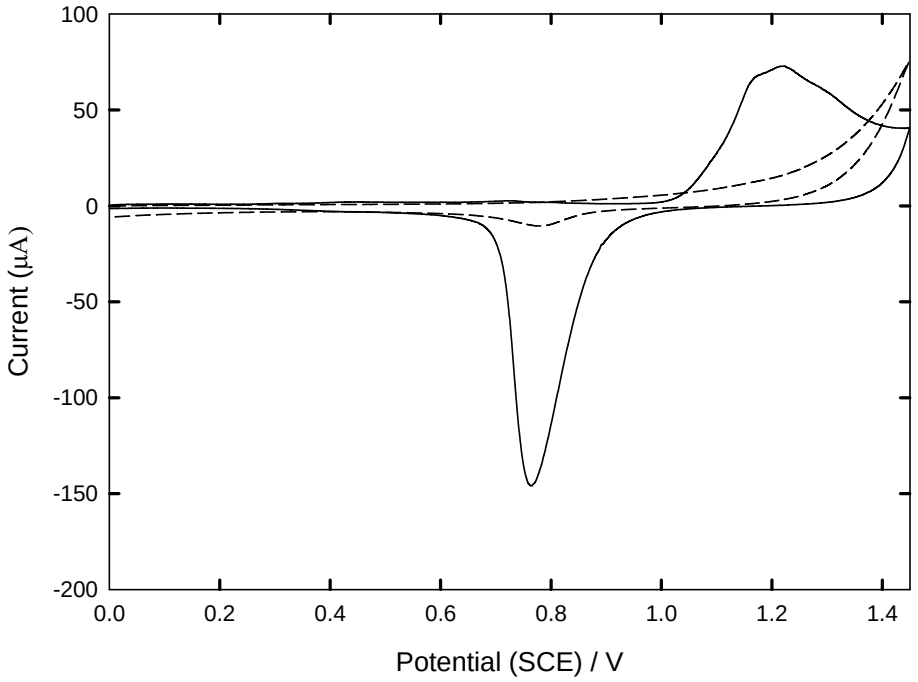

Figure 4: Voltammetric scan in 0.01 M $HClO_4$, scan rate = 100 mVs^{-1}, showing the comparison in gold oxide formation and reduction of a bare (solid line) and modified (dashed line) surface.

The effects of applying a negative potential to a modified surface was examined to observe the stability of the film. It was well known that SAMs of thiols can be desorbed

from a gold surface by applying sufficiently negative potentials,[3] and it has been observed with diazonium derived films on carbon.[10] It was of interest to determine whether the same observation could be made for diazonium based films on gold surfaces. The effects of negative potentials on bare surfaces were also examined.

4.2.2.1. Effect of Negative Potentials on Gold Surfaces

The gold surface was prepared by flame annealing and potential cycling in 0.01 M $HClO_4$ for 2-4 hours, and a voltammetric scan of the bare surface recorded. The electrode was subjected to potential steps of (a) -1 V and (b) -2 V in 0.1 M $HClO_4$. The potential was held for 1 min, and then the electrode was removed from solution, rinsed, dried with nitrogen, and a voltammetric scan between 0 V and 1.45 V was obtained.

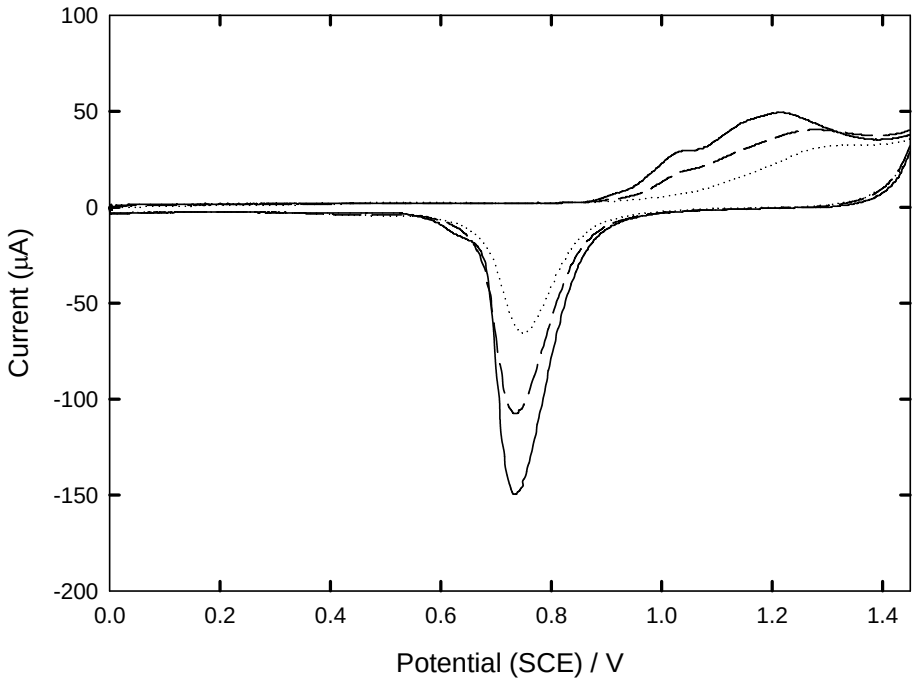

Figure 5: Voltammetric scans in 0.01 M $HClO_4$, scan rate = 100 mVs^{-1}, showing a bare gold surface:

freshly reconstructed (solid line), subjected to -1 V for 1 min (dashed line), and subjected to -2 V for 1 min (dotted line).

Several different behaviours were observed during the experiments involving application of negative potentials on a bare gold surface. An applied potential of -1 V has little effect on the oxide reduction peak and only a small decrease was observed. However potential steps to -2 V cause the peak to decrease significantly (Fig.5). However results were poorly reproducible. After this potential treatment, flame annealing the gold, followed by 10 min potential cycling was enough to bring the state of the gold oxides back to the initial stage. The reason for the irreproducible behaviour is not fully understood at present, but may be related the mobilities of gold atoms at the surface.

4.2.2.2 Effect of Negative Potential Steps on Films

After observing the effects that negative potentials had on the bare gold surface, negative potentials were then applied to films grafted to gold. The aim was to find a potential for stripping the films from the surface.

Initially the voltammetric scan of the bare gold electrode was obtained. Next the gold surface was modified with 1 mM diazonium salt in ACN with 0.1M $TBABF_4$. The modification peak was determined and an overpotential of -0.15 V was applied for 5 min, after which a voltammetric scan of the gold oxide reduction was obtained. After modification the electrode was rinsed, dried and put into 0.1 M $HClO_4$. The surface of the electrode was immersed fully into solution whilst nitrogen was bubbled through the

solution to remove any desorption products from near the electrode. The electrode potential was held at -0.5 V for 1 min, then the potential was then stepped progressively more negative at 0.5 V intervals between 0 V and -3.5 V. Each step was for 1 min. Voltammetric scans of the gold oxide reduction were obtained after each step.

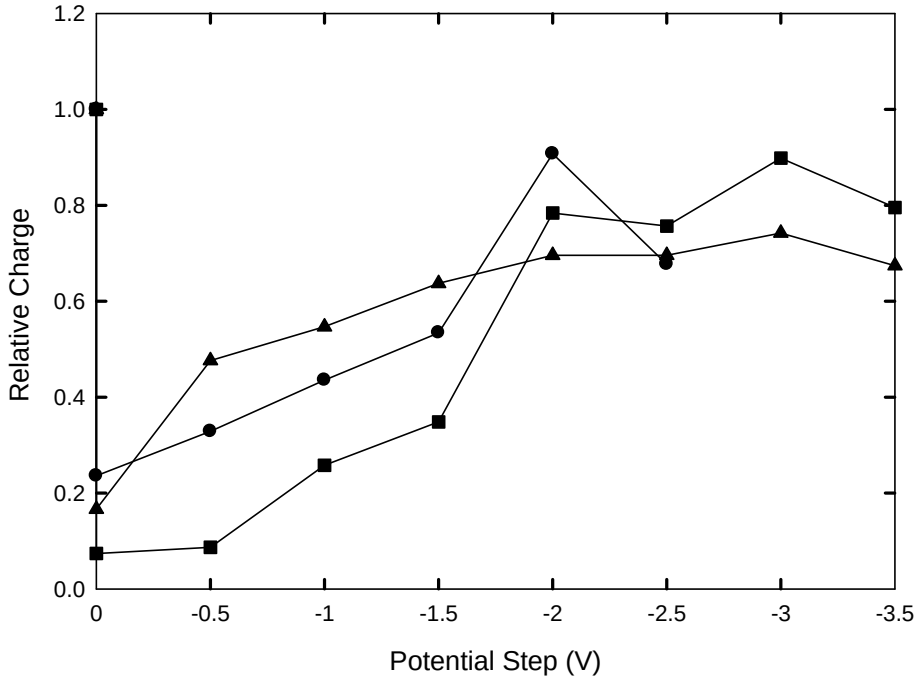

Figure 6: Relative charge for reduction of gold oxides after application of 1 min potential steps to 3 nitrophenyl modified gold electrodes. The relative charge is the charge measured after the potential step relative to charge measured after electrode reconstruction.

Following modification the amount of oxide formed at the surface significantly decreases (Fig.6). As the potential is stepped more negative, up to -2 V, the values of relative charge increase, indicating more gold oxide reduction is occurring. These results may be indicative of the film being removed from the surface as the potential applied to the film becomes increasingly negative. However after approximately -2 V the observed oxide

reduction peak began to behave erratically. Holding the potential at each step for longer periods of time resulted in little further change to the 1 min data.

Considering these findings alongside those for the bare gold surface (section 4.2.1.) indicates that potential steps to negative potentials cannot be used to strip film from the surface or to assess the amount of film at the surface. The bare gold surface is largely unaffected by steps to -1 V, but Fig. 6 shows that the film remains on the surface at -1 V. The bare gold surface is affected by steps to -2V, and both the bare surface and modified surface behave irreproducibly at that potential.

4.2.2.3 Effect of Potential Cycling on Films Grafted at Gold Surfaces

Films that are formed at a gold surface have been shown to block the formation of gold oxide.[9] A surface was prepared and modified with either, the methylbenzene or carboxybenzene diazonium salt, as mentioned previously in the work. Films were grafted for 1 min and 5 min. Voltammetric scans of the oxide reduction were taken before and after the modification. The surface was then subjected to potential cycling in 0.01 M $HClO_4$ at $\upsilon = 100$ mV s^{-1}. Further voltammetric scans taken after every 2^{nd} cycle from 0-20 cycles, then every 5^{th} cycle from 20-50 cycles and finally every 10^{th} cycle from 50-100 cycles. From the charge associated with the reduction of the gold oxide the maximum coverage of the film can be established.

To observe any gold oxide formation and reduction at a modified gold surface, there has to be pores or channels in the film extending from the bulk solution to the surface. This structure may be a result of only partial film coverage given by a poorly grafted film. Voltammetric scans showing the oxide reduction of a modified surface will hence give a picture of how well the surface is covered by a deposited film. Fig. 7 shows the relative charge associated with gold oxide reduction of a modified gold surface as a function of the number of potential cycles in 0.01 M $HClO_4$. As expected, it can be seen that modification for 5 min with both films leads to a large decrease in the relative charge associated with gold oxide reduction indicating the presence of a grafted film. The 5 min methyl film exhibits 60 % apparent film coverage, whereas the carboxyl film exhibits 50 % apparent coverage. As the film is continually cycled the amount of oxide reduction increases, and by estimating the final steady state, a surface coverage of approximately 12 % is determined.

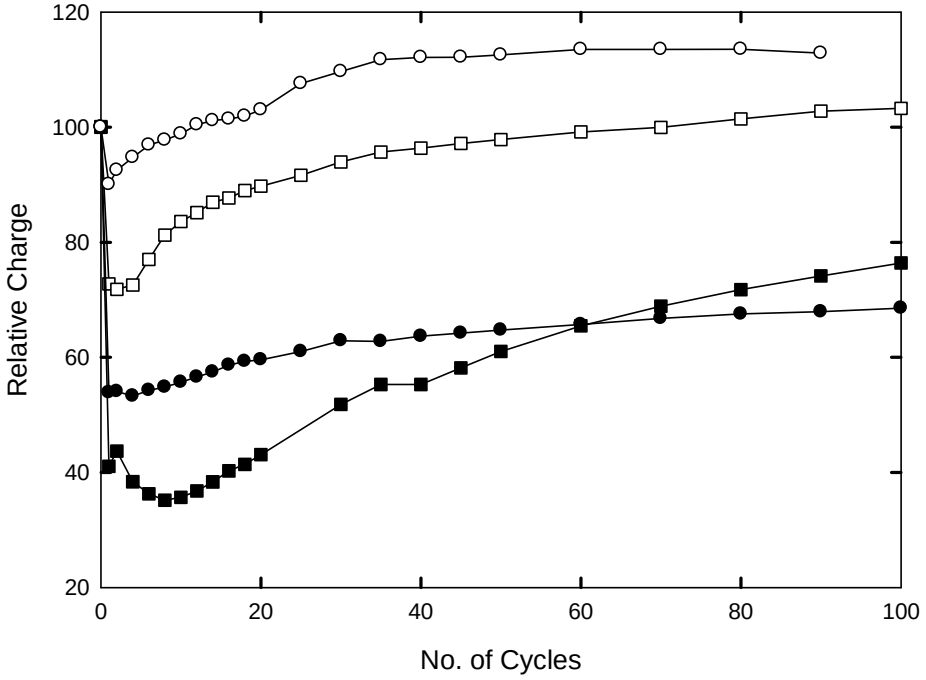

Figure 7: Plot showing the effect of potential cycling on methylphenyl (■) and carboxyphenyl (●) films at a gold surface. Films were grafted at 1 min (open symbols) and 5 min (closed symbols). The initial bare surface is at cycle 0, with modification at cycle 1. Potential cycling was undertaken at 50 mVs^{-1} in 0.01 M $HClO_4$.

The gold oxide behaviour after modification indicates that many gold atoms are still free to form oxide. The surface coverage of gold oxide at a bare reconstructed gold surface can be calculated by Equation 1, using the average charge required to reduce a monolayer of oxide at a polycrystalline interface of 400 μC cm^{-2} (Chapter 3):[11]

(1) $$\Gamma = \frac{Q_{ox}}{nF}$$

Here Q_{ox} is charge density, n is the number of electrons involved in the reduction, and F is Faraday's Constant. Given the reduction of gold oxide requires 3 electrons, the

coverage of gold atoms at the surface can then be calculated. From this $\Gamma = 1.4 \times 10^{-9}$ mol cm^{-2} is determined to be the coverage of gold atoms at the reconstructed surface.

Steady state relative charge values of approximately 30 % for carboxyphenyl and methylphenyl films corresponds to a maximum surface coverage of approximately 4.3×10^{-10} mol cm^{-2}. This is the surface coverage of phenyl groups directly attached to surface gold atoms. By measuring the charge associated with reduction of nitrophenyl groups grafted to carbon electrodes, a surface concentration per monolayer equivalent of $\Gamma = (2.5 \pm 0.5) \times 10^{-10}$ mol cm^{-2} has been reported.[8] The value obtained in this work is in reasonable agreement to that value and suggests a similar film grafting process at gold and carbon i.e. formation of a covalent bond between the surface and modifier.

Carboxyphenyl and methylphenyl films grafted for 1 min give a decrease in relative charge by 10 – 30 %. The smaller change to relative charge compared to 5 min films is expected at shorter times. However, after potential cycling the amount of oxide reduced becomes greater than oxide formed at the initial surface i.e. relative charge > 1. This occurs after about the 10^{th} and 70^{th} cycle for the carboxyphenyl and methylphenyl films, respectively. The results obtained can be accounted for by the pre treatment of the gold surface. For these experiments, the surface had only been piranha treated and flame annealed before modification, but no potential cycling and surface reconstruction was undertaken. Hence during the subsequent potential cycling the surface undergoes reconstruction. As more gold atoms are able to undergo oxidation, Relative charge becomes larger than 1.

4.2.3. Effect of Sonication on Films Grafted to Gold Surfaces

4.2.3.1. Electrochemistry of $Fe(CN)_6^{3-/4-}$

Cyclic voltammetry of $Fe(CN)_6^{3-/4-}$ can be used to observe the properties of films at a surface. Electron transfer from solution to a bare surface is not blocked and a well defined probe response is observed.[9] However if a surface has been modified with a film, then the electron transfer may be blocked by the film, and the probe response is diminished (Fig.8). If the film is not conducting and there are no pin-holes, pits or defects in it, then electron transfer will be successfully blocked. However if the film is thin or is porous in nature, then electron transfer can still occur between the $Fe(CN)_6^{3-/4-}$ and the gold surface, albeit at a slower apparent rate than at a bare surface. This can be observed in the voltammetric scans as decreases in the peak currents, and shifting apart of the peaks.

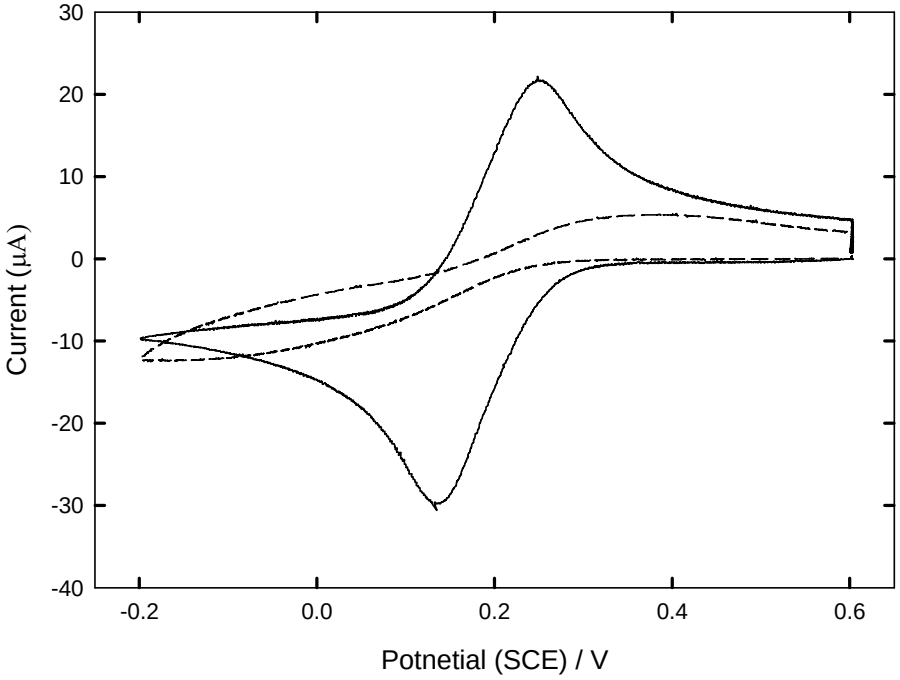

Figure 8: Voltammetric scans of 5 mM $Fe(CN)_6^{3-/4-}$ in phosphate buffer solution, 0.1 M KCl, scan rate = 100 mVs^{-1}, probe showing the comparison between a bare (solid line) and a methylbenzene modified (dashed line) gold surface.

There are some difficulties with the information obtained from redox probes. It has been seen that changes in the probe response that would indicate film desorbing from the surface under specific treatments, are not supported by AFM or XPS measurements of the film structure. This reveals that the loss of the modified electrodes ability to block electron transfer can't be equated with loss of the film from the surface.[12]

Film grafting methods use sonication to clean surfaces after grafting, and sonication in solvents for prolonged periods of time have been suggested to strip the film from the surface, whereas others suggest the film is still present after sonication.[9] Therefore the

effect of sonication of the methylphenyl and carboxyphenyl films in different solvents was examined, with voltammetric scans of $Fe(CN)_6^{3-/4-}$.

The gold surface was prepared by flame annealing and potential cycling in 0.01 M $HClO_4$ for 3 hours and a voltammetric scan of $Fe(CN)_6^{3-/4-}$ at the bare surface was obtained (Figs.9,10 solid lines). Next the surface was modified for 5 min with either the methylphenyl or carboxyphenyl film as described previously. Following modification, the surface was rinsed with ACN and a voltammetric scan was obtained of the redox probe at the surface. The modified surface was then immersed in specific solvents and sonicated for a known time, removed, rinsed, dried with nitrogen, and then a redox probe scan was taken of the modified surface. This electrode was repeatedly immersed in different solvents, sonicated and a redox probe voltammogram obtained.

Initially a gold surface was modified with a methylphenyl film, and sonicated in first ACN and then Milli-Q water. Voltammetric scans of $Fe(CN)_6^{3-/4-}$ showed a successful modification occurred, as the electron transfer was visibly blocked. After sonication in ACN, a voltammetric scan showed much less blocking of electron transfer, suggesting that the film had desorbed from the surface. However, the surface was then sonicated in Milli-Q water, and the probe response became more blocking towards electron transfer, indicating that the film was still there and desorption had not occurred. This process was observed to be reversible. However no temperature control was used in these experiments and the results showed poor reproducibility. The sonication process is very energetic and throughout this step the waterbath was noted to gradually heat up. For this reason the

following experiments were repeated with temperature control. Temperatures of either 45 ºC or 0 ºC were used for all experiments.

The redox probe scans show the methylphenyl film became less blocking to electron transfer after sonication in acetonitrile, and more blocking after sonication in water (Fig.9), whereas with the carboxyphenyl film, the redox probes show less blocking behaviour after sonication in water and more blocking after sonication in pet ether.

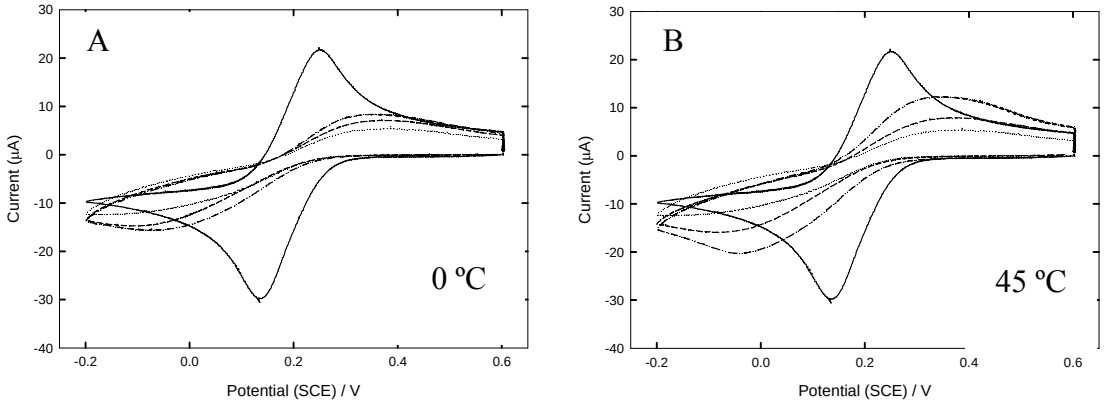

Figure 9: Voltammetric scans of 5 mM $Fe(CN)_6^{3-/4-}$ in phosphate buffer solution, 0.1 M KCl, scan rate = 100 mVs^{-1}, at a bare gold surface (solid line), and a gold surface modified with a methylphenyl film (dotted line), after sonication in water (dashed line), and after sonication in ACN (dashed/dotted line). Temperatures of 0 ºC (A) and 45 ºC (B) were used.

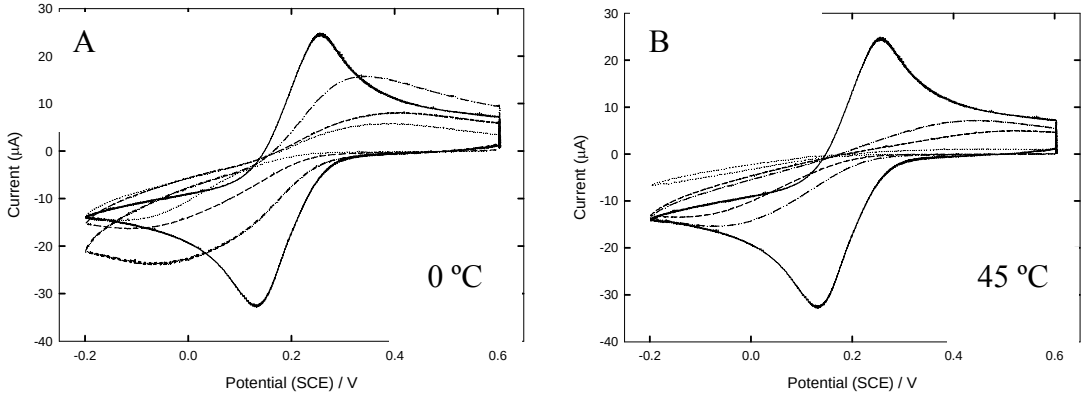

Figure 10: Voltammetric scans of 5 mM $Fe(CN)_6^{3-/4-}$ in phosphate buffer solution, 0.1 M KCl, scan rate = 100 mVs^{-1}, at a bare gold surface (solid line), a gold surface modified with a carboxyphenyl film (dotted line), after sonication in PE (dashed line), and after sonication in water (dashed/dotted line). Temperatures of 0 ºC (A) and 45 ºC (B) were used.

The reasons for this behaviour arise from the film structure. The voltammetric results obtained from the methylphenyl film after sonicating in acetonitrile and water suggest that the film swells and compresses due to the differing hydrophobicity between methylphenyl film and the solvent. Sonication in the polar hydrophilic solvent, water, causes the methylphenyl film to shrink and become less porous, therefore more blocking towards electron transfer to the redox probe. On the other hand sonication in ACN causes the film to swell, exposing pinholes and defects in the layers. This in turn enables a faster apparent rate of electron transfer.

The observed redox probe scans of the freshly modified surface before sonication were not recoverable, suggesting that there must be a small amount of unbound diazonium salt or electrolyte ions trapped within the film, or weakly adsorbed to it, that are released after sonication. Reversible changes are seen in the following redox scans after sonication in

different solvents at each of the methylphenyl and carboxyphenyl interfaces. Redox probes revealed that increased temperature of the solvent gave faster electron transfer for the same period of sonication time as in colder solvents.

It is clear from these experiments that the trends were the same at both temperatures. Associating wholesale loss of film with faster redox probe response after sonication is not necessarily valid. Redox probe scans after further sonication in solvents of different polarity or hydrophilicity provide evidence that the film is still present.

4.2.3.2. Contact Angle Measurements

The purpose of water contact angle measurements is to observe the wettability of the surface. Contact angle measurements of films grafted to gold and after sonication were used to identify hydrophobicity changes at the surface and to correlate these with redox probe results. The modified surface exhibits a different contact angle value to the unmodified surface. The hydrophilic properties of the film will effect the magnitude of the contact angle. Hydrophobic surfaces are generally considered to exhibit an angle greater than 65 º, whereas a hydrophilic surface will exhibit an angle smaller than 65 º. Additional factors such as surface roughness/topography and the structure of the film also effect the measured value of the contact angle.

4.2.3.2.1 Contact Angle Measurements at Bare Gold Surfaces

The contact angle of bare gold was measured after sonication in ACN, PE and Milli-Q water (Fig.11). A bare gold surface was found to have a contact angle of 85 ± 5 º. The contact angle of bare gold did not change significantly after sonication in PE and Milli-Q water. However, a large change was observed after sonication in ACN. This may arise from the energetic sonication process causing ACN molecules to adsorb to the surface. The adsorbed species will in turn affect the observed contact angle of the gold surface.

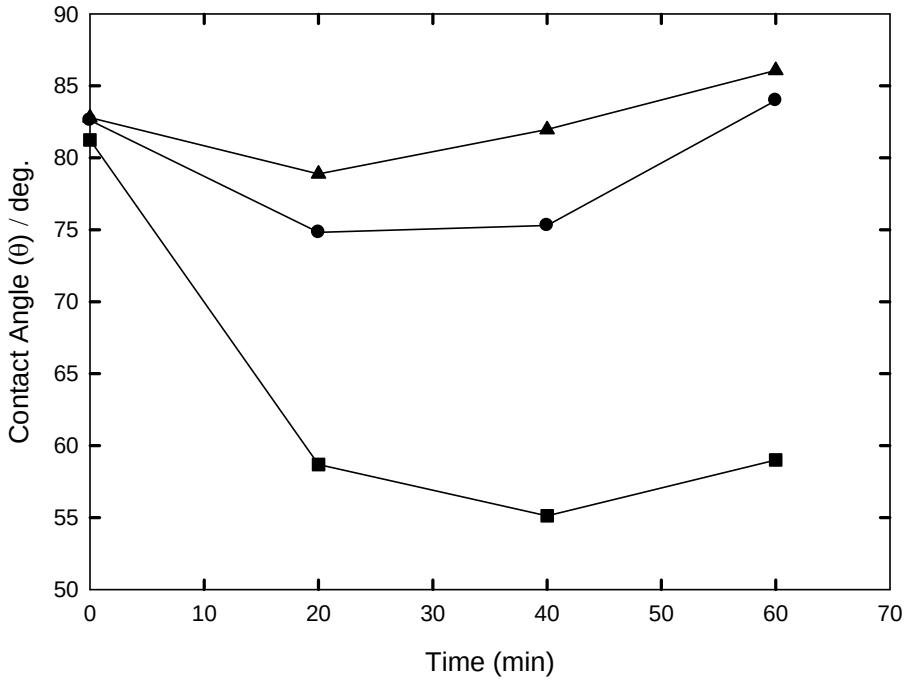

Figure 11: Effect of sonication on the contact angle of a gold surface in different solvents. (■) represents gold sonicated in ACN, (●) represents gold sonicated in PE, and (▲) represents gold sonicated in Milli-Q water.

4.2.3.2.2. Contact Angle Measurements at Modified Gold Surfaces

Freshly prepared gold surfaces were modified with methylphenyl and carboxyphenyl films that were grafted electrochemically as described previously by stepping to an overpotential of -0.15 V past the modification peak. The applied potential was held for 1 or 5 min to achieve either a thin or thick film. Contact angles of the bare gold surface and the modified surface were then measured. These surfaces were subjected to the same sonication procedures as for films grafted to the polycrystalline surface used for redox probe studies. Methylphenyl films were sonicated for 20 min in ACN and then 20 min in Milli-Q water. Carboxyphenyl films were sonicated for 20 min in Milli-Q water and then 20 min in PE. Contact angles were measured after each sonication step. The sonication process was performed by alternating between these solvents to determine whether the process was reversible.

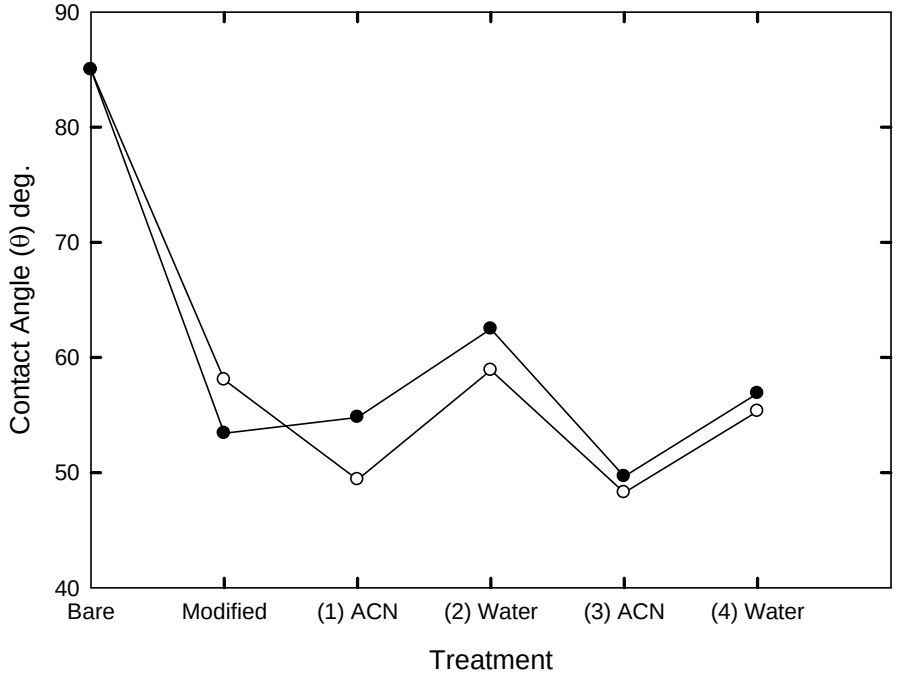

Figure 12: Contact angle measurements of 1 min (○) and 5 min (●) deposited methylphenyl films immediately after modification and after sonication in ACN and Milli-Q water for 20 min periods at 0 ºC. The numbers indicate the order of the sonication experiments.

The effect of sonication on the contact angles for a methylphenyl film sonicated in ACN and Milli-Q water were shown in Fig.12. The contact angle of the bare gold surface is 85 º ± 5 º. Immediately after modification the freshly prepared film was rinsed and the contact angle of the surface measured. There is a decrease to 58 ± 2 º for a 1 min methylphenyl film and 53 ± 2 º for a 5 min methylphenyl film. The change to the contact angle shows the Au surface was successfully modified. Upon sonication in ACN, the contact angle changes from 58 ± 2 º to 50 ± 2 º for the 1 min film and from 53 ± 2 º to 54 ± 2 º for the 5 min film. The contact angle subsequently increases after sonication in water, and decreases following sonication in ACN. This is due to the hydrophobic

difference between the methylphenyl film and the solvents. After sonication in water the film will compress presenting a more hydrophobic interface. After sonication in ACN the film swells, as described for the redox probe scans carried out on gold surfaces under the same conditions. This explains the reversibility observed, and would confirm the suggestion that that film compression and swelling occurs after sonication in solvents of different polarity.

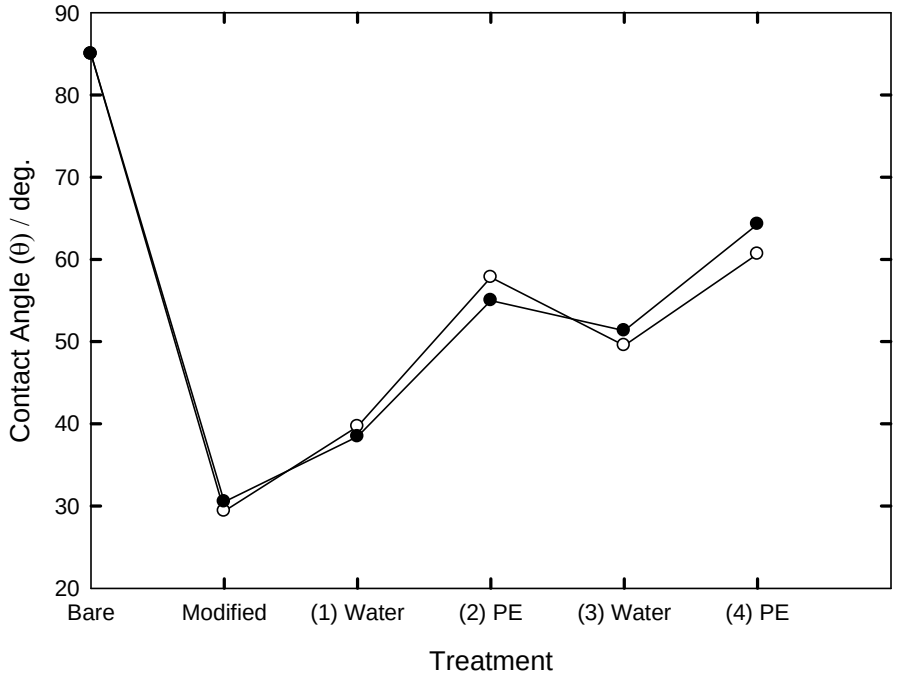

Figure 13: Contact angle measurements of 1 min (○) and 5 min (●) deposited carboxyphenyl films immediately after modification and after sonication in PE and Milli-Q water for 20 min periods at 0 ºC. The numbers indicate the order of the sonication experiments.

Modification of the gold surface with the carboxyphenyl film gives a contact angle of ~ 30 ± 2 º for films electrochemically grafted for 1 and 5 min (Fig.13). Sonication in water further increases the contact angle to 40 ± 2 º. Further sonication in PE gives a further

increase in the hydrophobicity of the surface to 55-58 ± 2 º. After the sonication in water the contact angle again decreases. The observed results of the sonication of the carboxyphenyl film in solvents of different polarity and hydrophobicity are similar to those of the methylphenyl film. After sonication in water, the film appears to swell but after sonication in PE the film appears to compress. The carboxyphenyl film is more hydrophilic than the methylphenyl film, so it is expected to exhibit the opposite behaviours to sonication in similar solvents.

The contact angle measurements support the results obtained for redox probe scans at methylphenyl and carboxyphenyl modified gold surfaces. Film structure appears to be changing after sonication in solvents of different polarity. It is assumed that the films are trying to maximise the number of either the functional groups or the phenyl groups during sonication depending on the nature of the solvent. For example, carboxyphenyl films after sonication in water exhibit a smaller contact angle, indicating a surface hydrophilic in nature. But after sonication in PE the interface exhibits a larger contact angle, indicating a more hydrophobic surface. The results observed in this experiment may be utilised in preparing surfaces with pre-determined wettabilities for other applications.

4.2.3.3 Effect of Sonication on Gold Oxides after Modification and Potential Cycling.

Carboxyphenyl and methylphenyl films were grafted for 5 min to polycrystalline gold surfaces as described previously. The modified surface was then cycled 100 times in 0.01

$HClO_4$ so as to reconstruct the unmodified gold atoms remaining at the surface. The surface was then sonicated in Milli-Q water at 0 ºC. Sonication times of 5, 10, 20, 40 and 60 min were chosen .Voltammetric scans of the gold oxide reduction were obtained before and after modification as well as after potential cycling, and after each sonication step. Fig. 14 shows the relative charge for reduction of gold oxides as a function of electrode treatments.

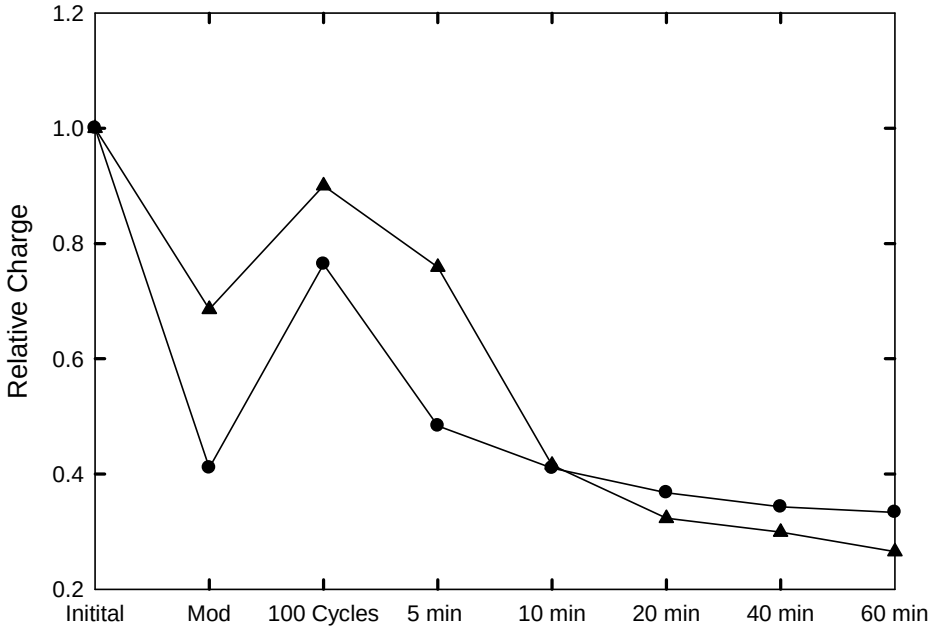

Figure 14: The effect of sonication in Milli-Q water on methylphenyl (●) and carboxyphenyl (▲) modified gold surfaces. After modification the electrode was cycled 100 times in 0.01 M $HClO_4$ prior to sonication.

The amount of oxide that is formed at the surface decreases dramatically after modification as expected. The amount of methylphenyl and carboxyphenyl film grafted to the surface is very similar to that noted previously is section 4.2.2.3, with coverages of approximately 60% and 30% respectively. After potential cycling the relative charge has

increased to 80% and 90% in each case, again similar to what was seen before in section 4.2.2.3.

Fig. 14 shows that after prolonged sonication the relative charge decreases for both films to 30%. This behaviour is similar to that of a bare surface as seen in section 2.5 of Chapter 3. As sonication of a surface with a grafted film is similar to that of a bare surface, it can be assumed that the mobility of the gold atoms at the surface remains relatively unchanged. This would be expected of a surface where the grafted film only comprises approximately 20% coverage, as the properties of the bare gold are still predominantly visible.

4.3. Conclusion

Gold surfaces were modified by the electrochemical grafting of diazonium salts. The modified surfaces were subjected to sonication and solvent treatments to investigate film stability and structure. Redox probes and water contact angle measurements were used to examine the film-solution interface.

Examination of a freshly modified surface through gold oxide reduction methods indicated that methylphenyl and carboxyphenyl films grafted to gold only comprised about 30 % of the surface. This indicates that the surface is largely vacant and the film porous in nature, with solvent and ions inhabiting the spaces between the film. Sonication

of the modified surface had significant effects on the gold surface, and further attempts to characterise the film through oxide reduction measurements was impossible.

Redox probes and contact angle measurements were obtained for methylphenyl and carboxyphenyl modified surfaces that had been sonicated in different solvents. These films exhibit reversible behaviour to sonication in solvents of different polarity and hydrophobicity. The films are flexible and the film-solution interface is able to change conformation with exposure to solvents of differing polarity.

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Chapter 5: Spontaneous Reactions of Aryldiazonium Salts with Gold Surfaces and Microcontact Printing

5.1. Introduction:

5.1.1. Spontaneous Reactions of Diazonium Salts and Conducting Surfaces

The previous chapter of this thesis describes surface modification entailing the use of electrochemical methods. However spontaneous reactions between the modifier and the substrate have been well documented, largely in the case of SAMs of thiols at surfaces such as gold or to a lesser extent platinum and paladium.[1,2,3,4,5] Diazonium salts have been seen to spontaneously react with a number of different surfaces such as carbon, silicon and iron.[6,7,8] The surface is assumed to act as a reducing agent that spontaneously reduces the diazonium cation. Open circuit potentials of metals have been measured and compared with the reduction potentials of various diazonium salts. It is apparent that the OCP of these metals is sufficient to spontaneously reduce many diazonium salts, especially the nitrobenzene derivative.[9] This gives rise to the aryl radical which will attach to the surface through a covalent bond, thus forming a film at the surface.

Spontaneous grafting is an easier way to modify surfaces as opposed to electrochemistry and much time and effort has been invested in developing new techniques for modification involving spontaneous reactions. Various nanofabrication techniques, such as microcontact printing utilise spontaneous reactions.

5.1.2. Microcontact Printing

Microcontact printing is a process that is based on spontaneous interactions at desired surfaces between substrate and modifier. It is normally used for the application of molecular patterns onto surfaces, which are employable in a wide array of applications such as, high density data storage, biotechnology and biosensors, and small scale circuitry.[10,11]

In the most common approach a gold surface is modified by stamping a thiol modifier onto the surface with the use of a polydimethylsiloxane (PDMS) stamp.[12] This stamp is inked with the modifier, and the stamping process transfers modifier to the surface where contacts are established (Fig. 1).[10] After the stamp has been removed, it leaves areas where the modifier is grafted to the surface, creating a pattern. If no pattern is present on the stamp surface the whole surface may be modified in this manner.

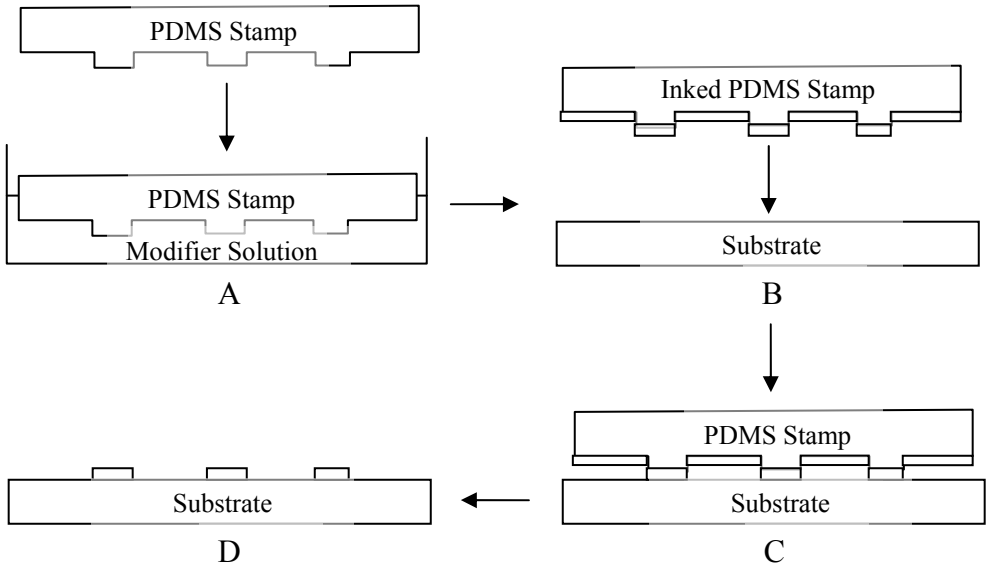

Figure 1: Schematic diagram of the microcontact printing process. Initially the stamp is inked in the modifier solution (A), then it is applied to the surface (B), stamped for a desired time (C), before finally removing to reveal the patterned surface (D).

Where a surface has been patterned it will exhibit new properties in micron scale regions. Resolution of these areas is limited by the surface diffusion of any printed molecules and any distortions occurring in the stamp during the printing process.

5.1.3. Monitoring the Spontaneous Reaction of Nitrobenzene Diazonium Salt at the Surface by Measuring the Surface Coverage of the NO_2 Functional Group

In this work the spontaneous reduction of nitrobenzene diazonium salt at gold surfaces is explored. The nitrobenzene diazonium cation is relatively easily reduced and hence is a good candidate for spontaneous reactions. Another advantage of using nitrobenzene

diazonium salt is that the surface coverage of a nitrophenyl film can be estimated by observing the electrochemical reduction of NO_2 groups to NH_2. This is a 6 electron process as shown in equations 1 and 2.[1,13]

$$(1) \quad Au\text{-}Ar\text{-}NO_2 + 4H^+ + 4e^- \rightarrow Au\text{-}Ar\text{-}NHOH + H_2O$$

$$(2) \quad Au\text{-}AR\text{-}NHOH + 2H^+ + 2e^- \rightarrow Au\text{-}Ar\text{-}NH_2 + H_2O$$

$$(3) \quad Au\text{-}Ar\text{-}NHOH \leftrightarrow Au\text{-}Ar\text{-}NO + 2H^+ + 2e^-$$

The reduction of NO_2 groups to NH_2 gives a characteristic voltammogram as shown in Fig. 2. This voltammogram of an electrochemically grafted surface was obtained in 0.1 M $NaClO_4$, water/ethanol (9:1 ratio), between the potentials of 0 and -1.2 V.[14] It is typical for this reduction to be observed at carbon surfaces in H_2SO_4 solution, however only hydrogen evolution can be seen in this medium at gold. A large reduction peak is observed that corresponds to the electroreduction of the NO_2 functional group to the NH_2. The second scan shows no reduction peak, indicating that all the NO_2 functional groups have been reduced.

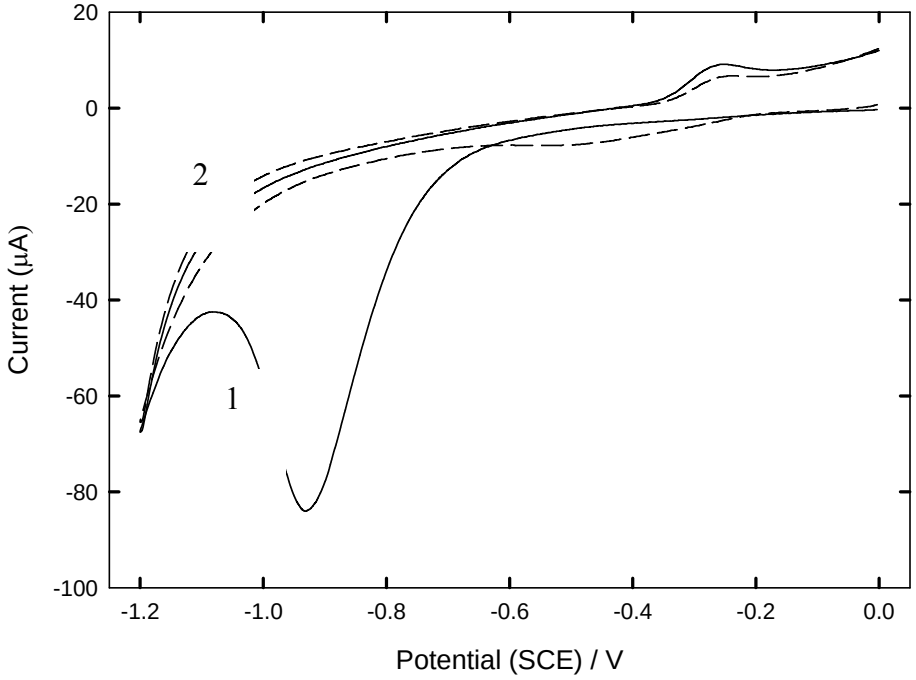

Figure 2: CV scan in ethanol/water (1:9), 0.1 M $NaClO_4$, scan rate 100 mVs^{-1}, showing the reduction of NO_2 groups to NH_2 amine groups on a gold surface electrochemically modified with a nitrophenyl film.

From the voltammetric scan of the NO_2 reduction it is possible to determine the surface coverage of the nitrophenyl film. The area under the peak can be obtained with the use of the curve fitting program Linkfit.[15] It can then be substituted into the formulae below to determine the actual concentration and hence surface coverage of the nitrophenyl film on the gold.

$$N_{NP} = Q_{peak}/Fn$$

$$\Gamma = N_{NP}/A$$

In the expression above, Q_{peak} is the charge associated with nitrophenyl reduction, which is determined by the area under the peak, (A.V)/ Vs^{-1}; n is the number of electrons (n = 6); N_{NP} is the number of moles of nitrophenyl groups; F = Faraday's constant. Finally surface coverage, Γ, is obtained by N/A where A is the electrode area. Units for surface coverage are mol cm^{-2}.[16]

Voltammetric scans of the reduction of NO_2 to NH_2 show a small oxidation process at -0.2 V and an associated broad oxidation at -0.4 V. During the reduction of NO_2, some groups are reduced by only 4 electrons (Eq. 1) and subsequently undergo a reversible redox reaction (Eq. 3). When calculating surface coverages these processes weren't taken into account (it was assumed that n = 6 for all nitrophenyl groups). In the majority of the printing experiments (see later) the 2 electron process was not observed. It can also be noted that due to the very small size of the peak corresponding to the 2 electron process when it was observed, only a small error of less than 5 % would arise from this assumption. Previous research using carbon surfaces demonstrated that the amount of NHOH formed is always minor.[17]

5.2. Results and Discussion

5.2.1. Spontaneous Reaction of Nitrobenzene Diazonium Salts in Solution with Gold Surfaces

The spontaneous reaction between the surface and aryldiazonium salt has not been reported in the literature for gold and hence is of interest for this research.

A solution of 10 mM nitrophenyl diazonium in deaerated ACN was prepared. The gold polycrystalline surface was first cleaned with piranha solution, flame annealed and potential cycled as described previously in the work, before being immersed in the modifier solution. A temperature of 20 ºC was maintained throughout the experiment and the electrode/modifier solution was left in a dark room to avoid exposure to UV light. After 1 hour the electrode was removed from solution and sonicated in deaerated ACN and acetone for several minutes. Voltammetric scans of the nitro reduction were then obtained (Fig. 2).[5,7]

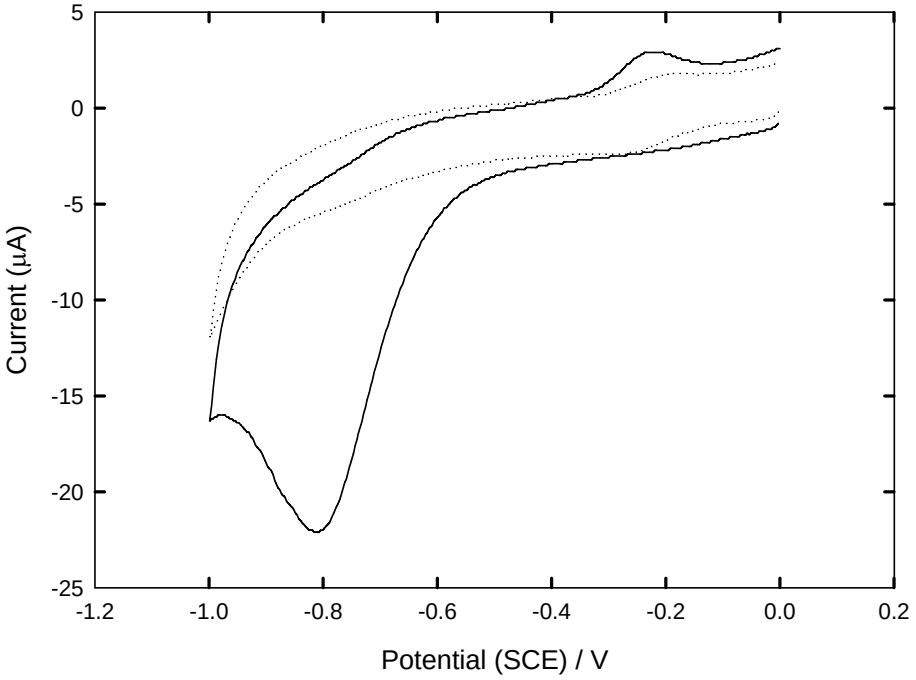

Figure 2: CV scan in water/ethanol (9:1), 0.1 M $NaClO_4$, scan rate = 100 mVs^{-1}, showing the reduction of NO_2 to NH_2 at a spontaneously grafted nitrophenyl film on gold.

Spontaneous grafting of diazonium salts was seen to be successful at gold. The first scan shows a sizeable nitrophenyl reduction peak, which is absent on the second scan, indicating that NO_2 groups at the surface have been successfully reduced. This voltammogram gives a calculated surface coverage of $\Gamma = 1.52 \times 10^{-10}$ mol cm^{-2}. Compared with a typical electrochemically grafted film (Fig. 3), where $\Gamma = 1.58 \times 10^{-9}$ mol cm^{-2}, the coverage is significantly lower at the spontaneously grafted surface.

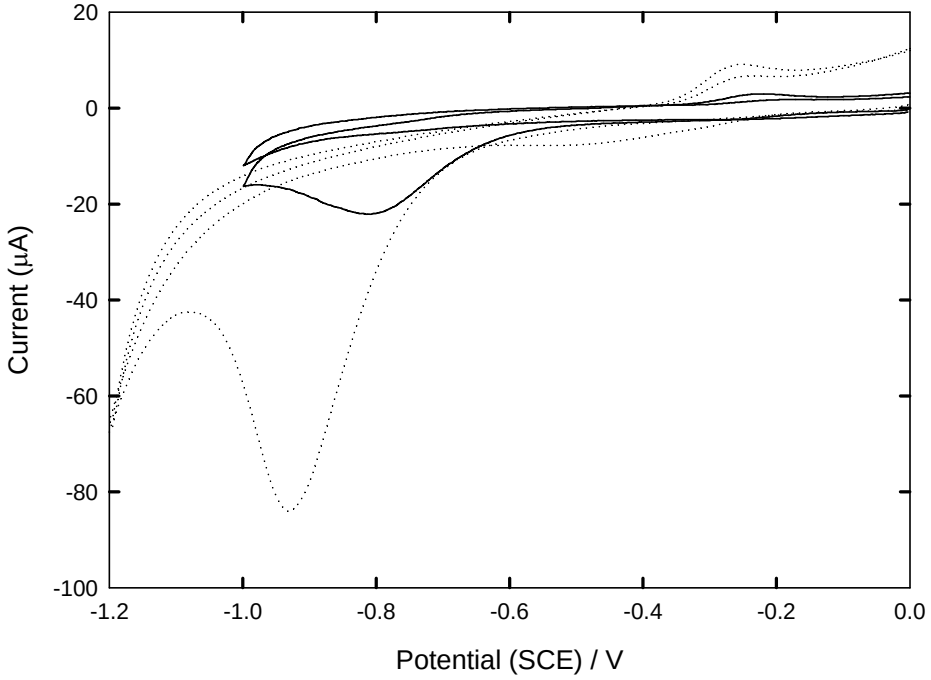

Figure 3: CV scan in water/ethanol (9:1), 0.1 M $NaClO_4$, scan rate = 100 mVs^{-1}, showing the reduction of NO_2 to NH_2 at an electrochemically grafted film (dashed line) compared to a spontaneously grafted film (solid line). Conditions used for the electrochemically grafted film were: 1 mM NB diazonium salt, 0.1 M $TBABF_4$, ACN, E_{app}= -0.2 V, t = 5 min. Conditions for spontaneously grafted film were: 10 mM NP diazonium salt, ACN, T = 20 ºC, no UV light.

It is surprising that spontaneous reactions appear to occur at gold, because the surface that the diazonium salt is grafting to is assumed to act as a reducing agent. However gold is not a strong reducing agent. It is possible that the diazonium cation is electrostatically attached to the surface during the reaction stage. When the electrode is transferred to the aqueous electrolyte to reduce the nitrophenyl groups, reduction of the diazonium cation could occur, leading to grafting.

5.2.2. Spontaneous Reaction of Nitrobenzene Diazonium Salts with Gold Surfaces During Printing

Observing the spontaneous reaction in solution suggested that modifier might be printed to the gold surface using an inked PDMS stamp. This reaction was investigated using a relatively large, non-patterned piece of PDMS which completely covered the area of the gold surface subsequently exposed in the electrochemical cell. The gold substrate used for the printing experiments, was comprised of gold adhered to silicon through a Ti or NiCr layer. DMF was used as the solvent for initial printing experiments. This solvent was previously shown to give excellent results when printing diazonium based modifiers on carbon substrates[18] and DMF has excellent compatibility with PDMS.[19]

Initial experiments demonstrated that printing films using diazonium salts was successful at gold surfaces. Further experiments were aimed at optimising the printing process. Several factors were examined including utilisation of varying degrees of stamp dryness after inking, the use of different solvents and the effect of applying weights during the stamping stage. The results of the printing experiments were investigated using the voltammetry of redox probes, electrochemical measurement of the surface coverage of nitrophenyl groups and by measurement of water contact angles.

5.2.2.1. Effect of Printing Time

Gold surfaces were printed as described in Chapter 2. A non-patterned stamp was inked with 20 mM diazonium salt in DMF for 1 minute. The stamp was dried under N_2 until all excess solvent appeared to be removed, and then the stamp was left to air dry for 30 s. Finally the stamp was gently applied to the surface for times of 5, 10, 20, 40, and 60 min. After the desired time the stamp was removed and the surface was ultrasonicated first for 20 s in acetone then for 10 s in IPA to remove any traces of solvent.

In electrochemical experiments the nitrophenyl reduction was not observed at all surfaces, and was only well defined at the surface printed for 20 min, where $\Gamma = 1.62 \times 10^{-10}$ mol cm^{-2}. This surface coverage is similar to that observed for the spontaneous grafting reaction in solution.

Table 1: Contact angle measurements of gold surfaces modified by printing with nitrophenyl diazonium salt. The contact angles were measured before and after reduction of the film in 0.1 M $NaClO_4$, water/ethanol (9:1 ratio). The contact angle of bare gold was 80-85º. All values are ± 2 º.

Printing Time (min)	60	40	20	10	5
Contact angle after printing (º)	86	79	57	84	83
Contact angle after reduction (º)	77	77	51	78	79

Printed surfaces were characterised by water contact angle measurements (Table 1). The data obtained for the contact angles reinforced the observations of the nitrophenyl film coverages. It can be seen that modification had very little effect on the contact angles of the surface. Apart from the 20 min print all the surfaces have contact angles similar to

bare gold (80-85º). Reduction in each case causes a small decrease in the contact angle which is expected when a nitrophenyl group is reduced to the more hydrophilic aminophenyl group. Contact angles obtained from nitrophenyl and aminophenyl films on PPF, are reported to be 64 ± 4 º and 46 ± 4 º respectively.[11] From these results it can be deduced that the printing has only given a very sparse coverage on the gold, allowing the underlying surface to influence the contact angle.

The surface printed for 20 min exhibited results closer to those expected for a complete coverage of a nitrophenyl film. It can be noted that the stamp for this surface had not been dried as thoroughly as the others. The presence of more solvent at the surface is likely to have caused a larger surface coverage, as more nitrophenyl diazonium salt is able to gain access to the surface to bind.

Voltammetric scans of $Fe(CN)_6^{3-/4-}$ were obtained for surfaces printed at times of 5, 10, and 20 min (Fig. 4) with the same printing technique as described above. The electrochemistry of $Fe(CN)_6^{3-/4-}$ is commonly used to characterise modified surfaces. As mentioned previously in Chapter 4, electron transfer occurs at the surface and if the transfer appears to be slowed at the treated surface then it may be deduced that a film is present. Recording probe scans is a simple and fast method for preliminary examination of modification reactions. However, films that have been grafted to surfaces by the spontaneous reduction of diazonium salts are reported as being sparse in nature and blocking of electron transfer is minimal at best. It is expected that similar behaviour will occur at gold.

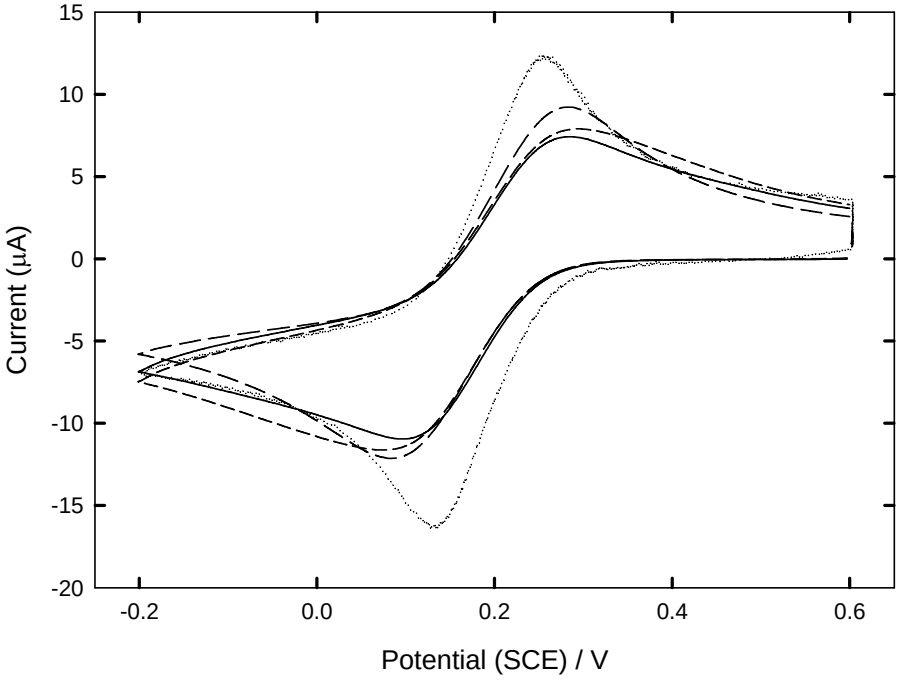

Figure 4: CV scans of $Fe(CN)_6^{3-/4-}$ in phosphate buffer solution, 0.1 M KCl, pH = 7, scan rate = 100 mVs^{-1} at: a bare surface (dotted line), a surface printed with 20mM NP diazonium for 20 min (large dashed line), 10 min (solid line), and 5 min (small dashed line).

The voltammetric scans obtained show that the surfaces modified by printing at each of the time intervals exhibit a small decrease in peak current and shifting of the peaks. However after printing with blank PDMS stamps (no modifier in the ink), voltammetric scans were very similar to those shown in Fig. 4. Hence the changes in voltammetric scans in Fig. 4 may be due to PDMS residues, and probe scans can't be used to give evidence for spontaneous grafting.

5.2.2.2 Effect of dryness of the stamp

In an attempt to increase the amount of grafted nitrophenyl groups a new technique for drying the stamps was initiated. After inking, the excess DMF was sponged off with a tissue, leaving the stamp still quite moist. The stamp was not dried with N_2, but left to air dry for periods of 30 s, 1, 2, 5, and 10 min. A printing time of 20 min was used as previous work had pointed to no significant change in surface coverage over the period of 10-60 min.

Surface coverages of $\Gamma = (4.5 \pm 1.5) \times 10^{-10}$ mol cm^{-2} were obtained for these surfaces. No overall trend was observed for film coverage with stamp drying time. The contact angle data also show no trend (Table 2). Surprisingly, contact angles were seen to both increase and decrease after reduction. Even though the contact angles of the modified surface were similar to what would be expected of an electrochemically grafted nitrophenyl film.[11] It is unclear why in some cases contact angles increase after electrochemical reduction.

Table 2: Contact angle measurements of gold surfaces modified by printing with nitrophenyl diazonium salt for 20 min. The contact angles were measured before and after reduction of the film in 0.1 M $NaClO_4$, water/ethanol (9:1 ratio). The contact angle of bare gold was 80-85º. All values are ± 2 º.

Drying Time (min)	0.5	1	2	5	10
Contact angle after printing (º)	70	57	64	68	62
Contact angle after reduction (º)	64	62	62	57	66

5.2.2.3. Effect of Reuse of PDMS Stamps when used for Printing DMF Based Inks.

Stamps cut from two different batches of PDMS were used in all the experiments, and were generally reused after cleaning in ethanol/water. To see if the 2 batches of PDMS give the same result and if reusing the stamps had an effect on the film printed at the surface, fresh and pre-used stamps were used to print nitrophenyl films onto gold surfaces and electrochemical reduction of the films was observed.

Film coverages obtained from reduction of the nitrophenyl films were $\Gamma = (4 \pm 1) \times 10^{-10}$ mol cm^{-2} for the pre-used stamps ($n = 3$), whereas a surface coverage of $\Gamma = (3.5 \pm 0.5) \times 10^{-10}$ mol cm^{-2} was determined for the fresh stamps ($n = 3$). This indicates that there were no significant differences between the two batches of PDMS stamp, and that the cleaning procedures implemented were working.

5.2.2.4 Effect of Ink Solvent

DMF is a good solvent to use with PDMS because it does not swell the PDMS and PDMS oligomers do not leach into the solvent.[16] Experiments were also undertaken with ACN because it was shown to be a satisfactory solvent for the spontaneous reduction of diazonium salts at gold. ACN has a similar PDMS compatibility rating to DMF.[16]

Using ACN as the ink solvent, the film coverages from the printing of gold surfaces were higher than those that utilised DMF as a solvent. Coverages of $\Gamma = 5\text{-}10 \times 10^{-10}$ mol cm^{-2}

were obtained. These coverages were significantly higher than those from surfaces that had been printed with DMF. Contact angle measurements (Table 3) showed no significant difference in printing time, or systematic changes after reduction of the nitrophenyl groups.

Table 3: Contact angle measurements of gold surfaces modified by printing with nitrophenyl diazonium salt in ACN. The contact angles were measured before and after reduction of the film in 0.1 M $NaClO_4$, water/ethanol (9:1 ratio). The contact angle of bare gold was 80-85º. All values are ± 2 º.

Printing Time (min)	60	40	20	10	5
Contact angle after printing (º)	79	74	70	67	65
Contact angle after reduction (º)	63	74	62	72	64

When using ACN as the inking solvent evidence for the leaching of unreacted diazonium salt from the PDMS was observed. Pre-used and fresh stamps were inked in ACN only (no diazonium salt), before being applied to gold surfaces. Electrochemical investigation showed a small amount of NO_2 reduction at surfaces modified by the pre-used stamps, whilst none occurred on surface that had been printed with the fresh stamps. The same experiment was carried out using DMF as the solvent, and no NO_2 reduction was seen with either pre-used or fresh stamps. This observation leads to the conclusion that diazonium salts were absorbed into the PDMS stamp after printing with DMF or ACN, and subsequent leaching occurred with ACN.

5.2.2.4. Effect of Shorter Printing Times and Surface Wetness

Microcontact printing at shorter time periods was examined, as longer times show little variation in coverage achieved. Printing times of 10, 7, 5, 2, and 1 min were used to print the gold surface with 20 mM nitrophenyl diazonium salt in either DMF or ACN. Film coverages showed no differences from surfaces that had been subjected to a longer printing time.

The comparison of surfaces that had been printed with dry stamps onto either a dry or wet surface was examined. After inking, the stamps were dried thoroughly with N_2 and left to air dry for 1 min. Gold surfaces that were dry or had a single 2 μL droplet of DMF or ACN on the surface were printed with the dry stamp. Film coverages obtained indicate that films deposited at wet surfaces had higher coverages of $\Gamma = (4 \pm 2) \times 10^{-10}$ mol cm^{-2} for both solvents, whilst dry surfaces had lower coverages of $\Gamma = (2 \pm 1) \times 10^{-10}$mol cm^{-2}. It can be deduced from these experiments that solvent facilitates grafting of films spontaneously to the surface through printing.

5.2.3. Patterning of Gold Surfaces by Microcontact Printing

As mentioned previously in this chapter, imparting patterns on surfaces via microcontact printing, will alter the properties of the interface in such a manner to create a functionalised surface for use in applications such as biosensors or molecular electronics.

Due to the success of printing nitrophenyl films onto gold surfaces, it was desired to see whether patterning of films can be achieved on the gold surface.

Initially patterning experiments were carried out using a PDMS stamp with a circular pattern, inked with 20 mM nitrophenyl diazonium salt in DMF. The stamp was inked and dried as described in the experimental chapter. Next the stamp was applied for 60 min. The printed surface was sonicated first for 20 s in acetone, and then for 10 s in IPA to remove any traces of solvent from the surface. SEM images were obtained (Fig. 5) revealing dark areas where the PDMS stamp had formed a contact with the surface. The lighter areas in Fig. 5 are bare gold.

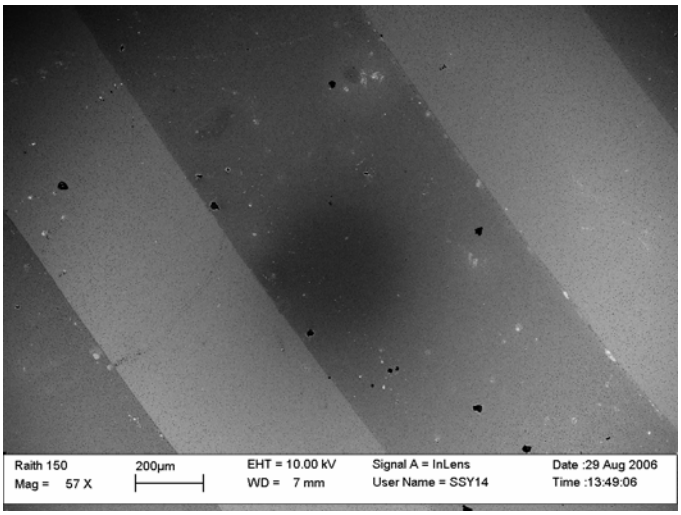

Figure 5: SEM image showing a gold surface patterned with nitrophenyl diazonium. The dark areas were in contact with the stamp diazonium and the light areas are bare gold. The stamp was inked with 20 mM NP diazonium salt in DMF, and the stamping time was 60 min.

The possibility that PDMS residues may give rise to the observed pattern was investigated. Two surfaces were compared where one stamp was inked with 20 mM

diazonium salt in either DMF or ACN, and the other stamp was inked with solvent only. Drying time was varied, to see how wetness of the stamp affected the print. Comparisons between a dry and a wet inking process were observed, to see how wetness of the stamp affects the pattern at the surface (Fig. 6-9). The dry method is the standard method described in the experimental chapter and wet printing involves sponging off the excess solvent without drying with N_2, leaving the surface moist.

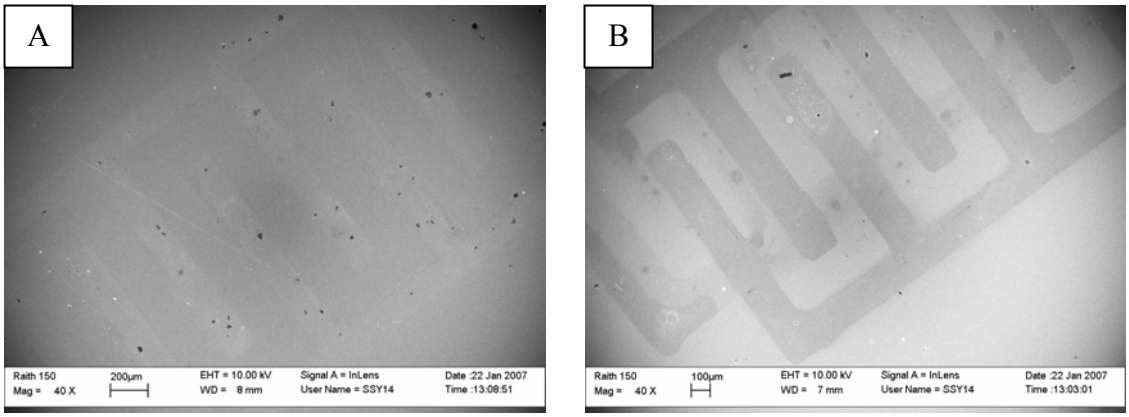

Figure 6: SEM images of patterned gold surfaces showing surfaces that have been stamped with (A) DMF only, and (B) 20 mM diazonium salt in DMF. The printing technique involved a dry stamping process and a time of 20 min.

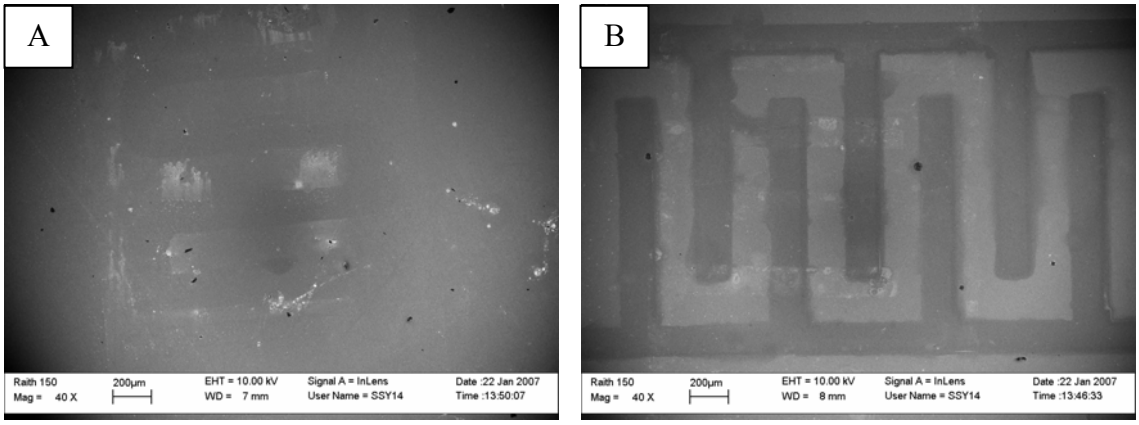

Figure 7: SEM images of patterned gold surfaces showing surfaces that have been stamped with (A) DMF only, and (B) 20 mM diazonium salt in DMF. The printing technique involved a wet stamping process and a time of 20 min.

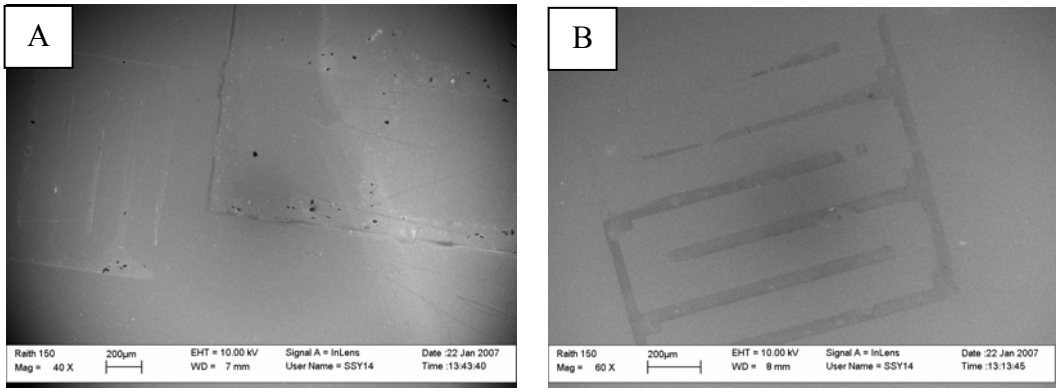

Figure 8: SEM images of patterned gold surfaces showing surfaces that have been stamped with (A) ACN only, and (B) 20 mM diazonium in ACN. The printing technique involved a dry stamping process.

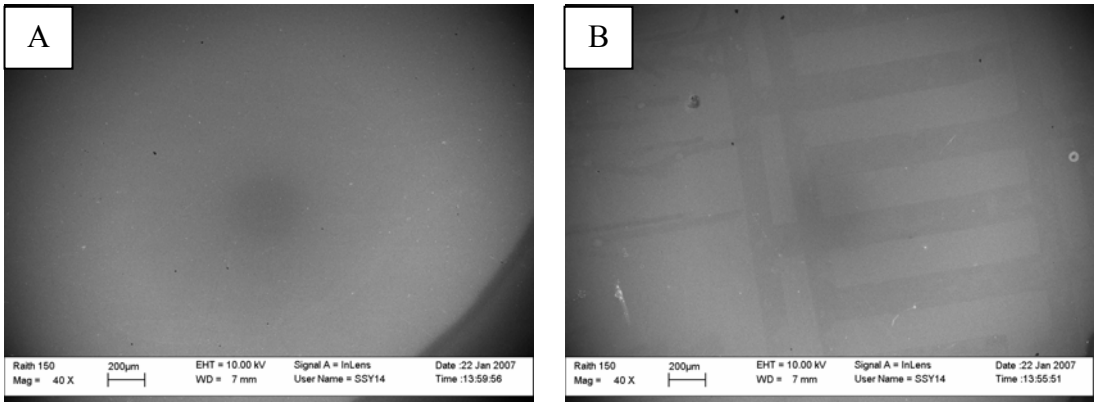

Figure 9: SEM images of patterned gold surfaces showing surfaces that have been stamped with (A) ACN only, and (B) 20 mM diazonium in ACN. The printing technique involved a wet stamping process.

In the absence of diazonium salt (Figs. 6-9 A), the areas contacted by the stamp are lighter than the bare gold, whereas in the presence of diazonium salt (Figs. 6-9 B), the areas contacted by the stamp appeared darker than the background. This provides further evidence that nitrophenyl groups are deposited at the surface without PDMS residues. It can be seen that patterning using DMF as a solvent gave much clearer patterns on the gold surface as compared with ACN. The surfaces that were printed with solvent only, have no dark areas, although a vague outline of the pattern can be seen in most images. This may be due to solvent or PDMS residues leaving traces on the surface, or it could be due to pressure of the stamp crushing the gold surface. The second explanation is more likely as in several images of the solvent printed surfaces, small pieces of gold have been lifted away from the surface upon removal of the stamp.

The dryness of the stamp also has an effect on the pattern printed on the surface (Fig. 10). It is observed that the drier DMF print gives a sharper pattern. Patterns with lines of widths of 200 µm, were observed after wet printing (Fig. 10 A), whereas line widths at

the drier interface (Fig. 10 B) were 100 μm. The excess solvent causes diazonium to be printed not only under the pattern but beyond the edges, reducing the sharpness of the print.

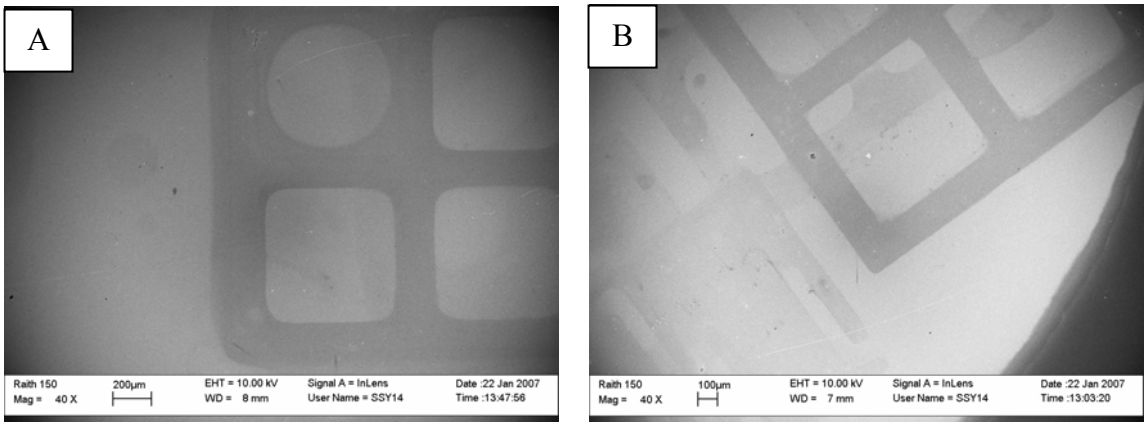

Figure 10: SEM images showing gold surfaces printed with (A) 20 mM nitrophenyl diazonium in DMF wet and (B) 20 mM nitrophenyl diazonium in DMF dry, both printed for a time of 20 min.

5.3. Conclusions

The spontaneous grafting of nitrophenyl diazonium salts to gold surfaces was observed and quantified. Spontaneous grafting gives only a fraction of the coverage that can be achieved through electrochemical methods. This is typical of spontaneous grafting at other surfaces. Spontaneous grafting at gold surfaces has not been shown in the literature before and is surprising because spontaneous reactions normally occur at surfaces such as iron, that act as strong reducing agents. The reaction needs to be examined further, to confirm that diazonium reduction does occur, rather than simple physisorption.

Grafting of nitrophenyl films through printing via soft lithography was also achieved. Films exhibited low coverages as would be expected, and a variety of different techniques were used to attempt to optimise the film coverage. The most important information from these experiments is that the grafting reaction is rapid (< 1 min) and that some solvent is required to achieve higher surface coverages.

Microscale patterning of gold surfaces with diazonium salts was examined. The use of different solvents (DMF or ACN) and drying techniques was utilised to observe how well the surface can be patterned. From SEM images, it was concluded that using DMF for the ink solvent, and a relatively dry stamping technique, provides well defined patterns on the surface. Using ACN as the solvent did not provide well defined patterns, and using stamps wet with either solvent gave poor resolution of the pattern.

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Chapter 6: Conclusions and Future Work

The modification of gold surfaces with aryldiazonium salts was investigated in this thesis. Properties of bare gold surfaces were observed to investigate the structure and stability of surface oxides. Gold surfaces were modified with different diazonium films and the stability and structure of these films examined. Spontaneous reactions between the gold surface and diazonium salts was also investigated with its potential application to printing and patterning of the surface

The preparation of a well formed gold surface is essential for electrochemical characterisation. However the high mobility of gold atoms at the surface makes the surface itself rather mobile, thus making observation of gold oxide electrochemistry difficult. Different solvents and ions can have profound effects on the surface structure. The structure of gold surfaces are prone to change due to the high mobility of gold atoms and the difficulty in obtaining a steady state for surface characterisation may lead to discrepancies in investigating gold oxide electrochemistry.

Gold surfaces were electrochemically modified with aryldiazonium salts. The structure and stability of these films was investigated with redox probes, gold oxide electrochemistry and water contact angle measurements. Methylphenyl and carboxyphenyl films were grafted to the gold surface, and gold oxide electrochemistry revealed that only a sparse surface coverage is achieved. Redox probes and contact angle measurements of modified surface were obtained, before and after sonication treatment in

solvents of varying polarity. The redox probes exhibited reversible changes after sonication in different solvents, indicating that total film loss is not achieved. These films derived from diazonium salts are flexible in nature, and able to alter the film-solution interface depending on the polarity or hydrophillicity of the solvent they are exposed to.

Spontaneous reactions between a wide variety of surfaces and diazonium salts have been well documented. However the spontaneous grafting of diazonium salts to a gold surface has not. The research in this thesis suggests that diazonium salts will bind to gold surfaces spontaneously to form covalently bound films. These films have a surface concentration much lower than electrochemically grafted films, suggesting only sparse coverage, as expected for a spontaneous reaction.

Printing of a gold surface via the technique of soft lithography was achieved using the spontaneous reduction of aryldiazonium salts. Electrochemical characterisation confirmed the presence of films derived from diazonium salts, at low surface concentrations, with little blocking of electron transfer, indicating a sparsely formed film. SEM images of surfaces patterned with nitrophenyl diazonium were observed. The results indicate that the surface has been successfully patterned with the modifier, and an optimal patterning technique was established.

The gold oxide electrochemistry of polycrystalline structures was thoroughly investigated in this research. Future work with gold could be focused at single crystal interfaces, in an attempt to observe how films derived from diazonium salts graft to smooth, planar

surfaces. Other factors such as the packing and orientation of the film on crystal faces with different indexes could be examined. It is easy to characterise gold surfaces with spectroscopic methods and techniques such as XPS, AFM, EQCM, IR and Raman spectroscopy could be employed to investigate film structure. The same methods may be employed in attempts to observe the Au-C bond suggested to be responsible for strongly grafted films. Further attempts to characterise the properties and relative stabilities of films formed from the diazonium salts other than those investigated in this thesis could be undertaken. Observation of how the diazonium concentration and solvent identity for electrochemistry effect the surface-film interface could be investigated. Modification of gold oxide instead of the bare gold surface could be attempted, and the structure and stability of these films also examined. This would most likely entail the use of spontaneous grafting as the low potentials for diazonium reduction would effectively reduce any gold oxide at the surface.

Spontaneous reduction of diazonium salts at gold surfaces has great potential. Further characterisation of this mechanism should be investigated, in particular to confirm that the diazonium cation is not simply physisorbed to the surface. The applications of the spontaneous reaction towards printing and patterning of gold surfaces can be expanded. It is important to further miniaturise the patterns derived from the spontaneous reduction of aryldiazonium salts. New techniques, inks and stamp compositions could be investigated, to try to find more effective ways to pattern gold surfaces with diazonium salts.